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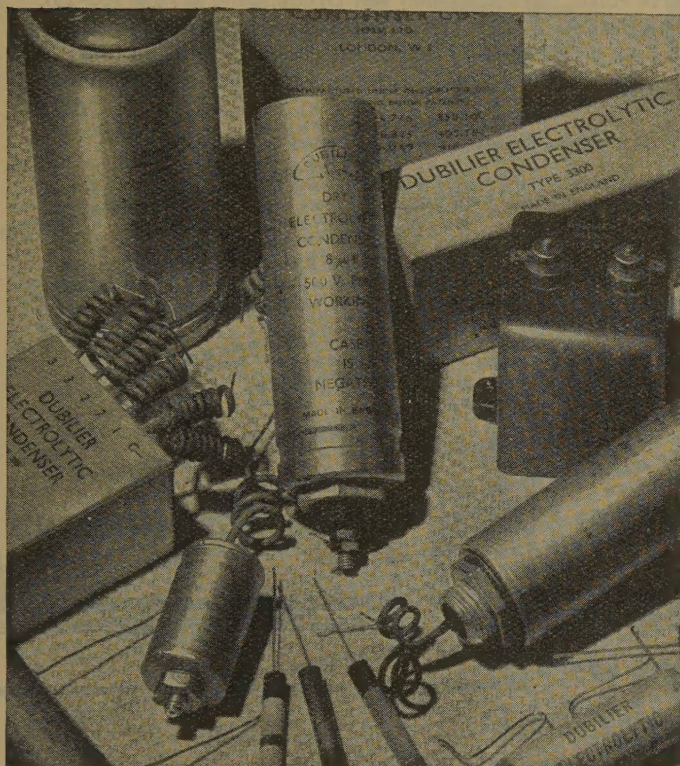
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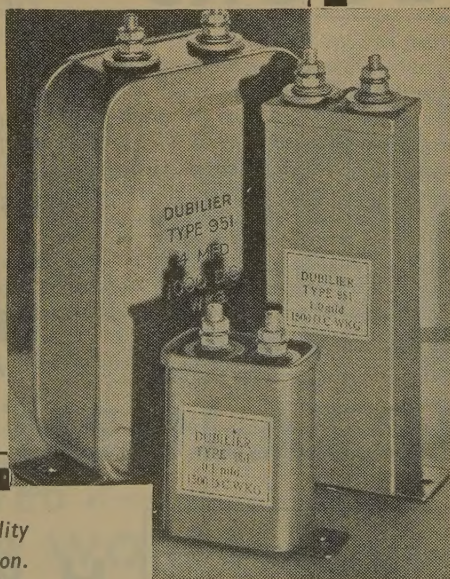
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SOME THERMAL AND ELECTRICAL ASPECTS OF THE DESIGN OF CONVERTERS FOR THE HYDRO- GENATION PROCESS

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ABSTRACT. A brief description is given of the hydrogenation process as applied to coal and tar, and some of the physical requirements in the design of apparatus and in the working of the process are enumerated. The final designs of converters with internal electric heating are described and a general account of the experiments carried out with a view to improving the thermal insulation, reduce the power consumption and decrease the temperature of the converter walls, is also given. The methods of maintaining a uniform temperature in the catalyst bed, and of dissipating the heat evolved by the reaction, which is strongly exothermic, are considered, and the experimental work is described. In the last section an account is given of the methods adopted to overcome the difficulties associated with electrical insulation.

§ 1. INTRODUCTION

IT may be of interest to members of the Society to have an account of the physical problems in the hydrogenation of tar and coal which have been encountered in experimental work at the Fuel Research Station.

When a coal is heated in a retort the complex molecules of the coal substance split up, yielding as main products of the carbonization (*a*) lighter hydrocarbon gases together with H_2 , CO , CO_2 and H_2S , etc.; (*b*) water which condenses as "liquor", containing a small proportion of ammonia, phenols, etc.; (*c*) tar, a mixture of heavier hydrocarbons, phenols, bases, etc.; (*d*) coke, which contains the greater part of the carbon present in the coal.

The quantity and composition of these products varies with the type of coal and the temperature at which the carbonization is carried out.

If, however, the coal is heated at about $450^\circ C.$, a temperature lower than that normally used in carbonization, in the presence of hydrogen at high pressure (about 200 atmospheres), destructive decomposition is avoided to a very large

extent. The primary products of decomposition, which at atmospheric pressure would decompose further or polymerize, are stabilized by hydrogenation. The result is that a large proportion of the coal substance is converted into oil.

When tar is treated with hydrogen, at 480°C . at a pressure of 200 atmospheres, a similar process occurs. The cracking which tar would ordinarily undergo at atmospheric pressure at this temperature is so modified by the presence of hydrogen under pressure, that the tar is converted into lower-boiling oils mainly hydrocarbon in nature. During the process the oxygen, nitrogen and sulphur in the raw material are converted into water, ammonia and hydrogen sulphide.

It has been found that the process of hydrogenation is much improved and accelerated by the presence of certain catalysts, of which tin is very effective for the treatment of coal, and molybdenum for the treatment of tar.

In the hydrogenation of coal, the catalyst in a powdered form is usually supplied to the converter as a constant proportion of the coal; only a very small amount of catalyst is required, and recovery is unnecessary. For the treatment of tar, however, a larger proportion of catalyst is needed. It has thus been found desirable to support the catalyst on a porous material through which tar and hydrogen are passed continuously. In this way, the necessity for recovering the catalyst is avoided. The catalyst-support which has so far been found most suitable is ignited alumina gel. This is impregnated with ammonium molybdate, which becomes converted during the hydrogenation process into molybdenum sulphide, the most active molybdenum catalyst⁽¹⁾.

A few typical results obtained by means of a single treatment of coal and low-temperature tar are given in table 1.

Table 1

Material	Coal	Low-temperature tar
Reaction temperature ($^{\circ}\text{C}$.)	450	450-480
Reaction pressure (atmospheres)	200	200
Yields of products (per cent by weight of raw material)		
Spirit boiling up to 200°C .	20	45
Oil boiling above 200°C .	57	44
Gas	8	8
Water	10	8
Unconverted coal (ash, etc.)	10	—
Hydrogen absorbed (per cent by weight of raw material)	5	5

The oil distilling above 200°C . may be re-treated and converted into light spirit, when it gives a total yield of motor spirit amounting to 65 per cent by weight of coal and 80 per cent by weight of tar.

The hydrogenation process must be conducted in a converter able to withstand very high pressures, but, for reasons explained later, the pressure vessel or converter must not, in a commercial process, be subjected to the full reaction temperature. Experiments have therefore been carried out at the Fuel Research Station with the

object of designing a converter heated internally by electrical means and so thermally insulated that while the reaction chamber is maintained at a temperature of 480°C . the walls of the converter do not exceed a temperature of 100°C . In the present paper descriptions are given of converters that have been evolved for the treatment of low-temperature tar, or distillates from high-temperature tar, under the conditions of temperature and pressure already mentioned. The principles involved and the experimental results obtained may also be applied to the design of a converter for the treatment of coal.

The earlier work at the Fuel Research Station was carried out in converters heated externally by means of gas or electricity. The wall of the converter was in consequence raised to the temperature of reaction. With ordinary steels there is a considerable reduction of strength at this temperature and this necessitates a much more massive construction to ensure the requisite factor of safety. More important, however, is the fact that hydrogen, at the high pressure and temperature employed, rapidly causes decarburization of the steel, leading to the formation of cracks which start from the inside of the converter and soon so seriously diminish its strength that replacement becomes imperative. This form of attack is described in a paper by Barber and Taylor⁽²⁾ which deals with the engineering side of this work at the Fuel Research Station.

The harmful results of hydrogen attack were reduced to a large extent by the use of certain alloy steels. Externally heated vessels are still therefore used for small-scale experimental work on the effect of various factors, such as temperature, pressure and time of contact, in view of the fine degree of temperature-control which it is possible to obtain in such converters.

The question of temperature-control raises several points of fundamental importance. The reactions occurring during the hydrogenation of tar are very susceptible to change in temperature, and, to a lesser degree, to change in pressure, and are markedly exothermic. The exact value of the exothermicity has not been determined because sufficiently accurate weight balances and calorific values of the raw materials and products are not at present available. It is hoped, however, to make some direct determinations of this heat of reaction in a specially designed converter-calorimeter. At present, from calculations based on the experimental observation that, when low-temperature tar is treated in an internally-heated converter, the heat of reaction is approximately equal to the heat required to raise the raw materials to reaction temperature, it is thought that the heat of reaction is of the order of 300 calories per gram of tar. Clearly the economic utilization of the heat of reaction, not accomplished in an externally-heated converter, is a vital consideration for a commercial process.

The requirements of a commercial process may now be summarized as follows. (1) The process should be continuous; (2) heat should be conserved as far as possible; (3) the temperature of the converter should be below that at which hydrogen attack becomes serious; and (4) the quantity and distribution of heat (and hence the reaction temperature) should be accurately controllable.

It was considered that these requirements would be satisfied by the use of an

electrically-heated cylindrical reaction chamber situated within a concentric pressure-resisting converter and thermally insulated therefrom. In the present paper the design of a suitable converter is described and some account of the difficulties encountered during its evolution is given also.

§ 2. DESIGN OF CONVERTER AND REACTION CHAMBER

Since the catalyst deteriorates gradually during use, it is necessary periodically to remove and reactivate it. It was thought desirable therefore that the arrangement of the converter should be such as to permit the removal of the catalyst without causing any disturbance to the heating units or the electrical connexions. In practically all the arrangements that were tried, it was accordingly adopted as an essential principle that the heating units should be wound on a cylindrical tube separate from the catalyst chamber. A satisfactory design incorporating this principle was evolved and is described below; a diagram of the arrangement is given in figure 1.

The converter, i.e. the outer, pressure-resisting vessel, is of mild steel 4 ft. long and 8 in. internal diameter. The walls are $1\frac{1}{4}$ in. thick and the flanges and end-covers respectively 1 ft. 4 in. in diameter and $3\frac{1}{4}$ in. thick. Mechanical details such

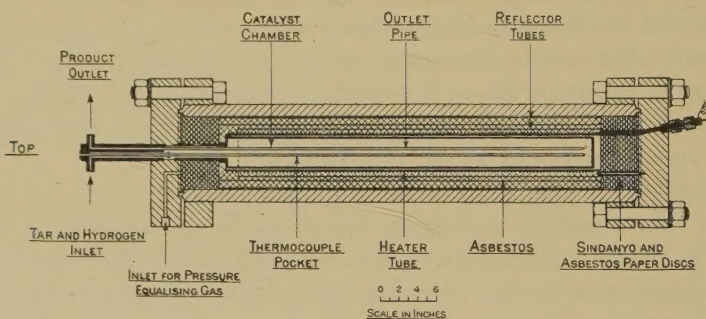


Figure 1.

as the method of making joints have been given elsewhere⁽²⁾. The catalyst or reaction chamber is also of mild steel and is 3 ft. 3 in. long and 3 in. in internal diameter; it is suspended from the top end-cover and hangs concentrically within the converter. Fixed eccentrically within the catalyst chamber are a thermocouple pocket and an outlet pipe for the reaction products, which pass down to the bottom. The pocket accommodates three thermocouples. Tar and hydrogen are fed into the top of the chamber through an annulus surrounding the thermocouple pocket and outlet pipe. Six radial metal conductors are placed within the catalyst bed and serve to assist in distributing the heat uniformly throughout the catalyst.

Surrounding the catalyst chamber, but not in contact with it, is the heater tube which is supported on, but electrically insulated from, the bottom cover. The tube is wound with three heating units, each of nine ohms resistance and consisting of no. 16 s.w.g. Brightray wire, and respectively 10, 20 and 8 in. long, the smallest being at the bottom and the largest in the centre. The heating units are insulated

from the tube by layers of mica and asbestos paper and are covered with fireclay. The electric current in each heater is controlled separately by means of external resistances. The electrical connexions, six in all, are carried through the bottom end-cover and insulated therefrom by a method to be described later. The annular space between the heater and the wall of the converter is filled with thermal insulation material consisting of asbestos paper wound on three concentric, cylindrical, chromium-plated brass tubes; the innermost of the latter fits closely on the insulation material wound on the heater. The ends of the catalyst chamber are insulated from the cover of the converter by means of pads of sindanyo and asbestos.

With this arrangement the catalyst chamber is completely isolated from the insulation space so that the latter is kept free from hydrocarbon gases and moisture formed during the reaction; earlier designs allowed the reaction vapours free access to the insulation space. For the purpose of maintaining equality of pressure the insulation space is connected by an external line to the hydrogen supply or other gas at the same pressure. It is not necessary, therefore, to construct the catalyst chamber as a pressure-resisting vessel.

In addition to good electrical and thermal insulation, the advantages of this apparatus are that the electrical connexions are made at the bottom cover and all the pipe connexions at the top, so that by lifting the latter the catalyst chamber may be withdrawn without disturbing the electrical heater.

As a modification of this type of converter, a further apparatus which has some advantages was designed and tested. This second converter differed mainly from the first in that the electric heaters were wound directly on the outer surface of the catalyst chamber and covered with half an inch of thermal lagging. By this device heat was applied more directly to the chamber, so that the heating element could be run at a lower temperature with consequently less deterioration of the electrical insulation. As the lagging over the heater was also increased by this arrangement, the thermal losses were reduced.

The catalyst chamber had the same internal dimensions as that used in the apparatus first described; the thermocouple pocket and the pipes for the introduction of tar and hydrogen and for the removal of products were similarly unchanged.

The advantages of this modified arrangement are that the power-consumption is reduced and the life of the electric heater increased; the disadvantage is that the removal of the catalyst chamber involves the removal of and possible damage to the heater. The relative importance of the advantages and disadvantages depends upon the nature of the process for which the converter is employed and particularly upon the frequency of replacement of the catalyst.

The throughputs of tar and hydrogen in these plants were normally 1600 ml. and 1700 litres per hour respectively. In certain runs made with approximately the same internal and external temperatures the tar rates were varied from 1200 to 2000 ml. per hour with corresponding rates for the hydrogen, and it was found that the same power input was required. It follows that the heat of the exothermic reaction is sufficient to heat the raw materials to reaction temperature; the electric power supplies the heat loss from the converter.

§3. PROBLEMS RELATING TO THERMAL INSULATION AND THE CONTROL OF TEMPERATURE IN THE CATALYST CHAMBER

Thermal insulation. A number of experiments were made on the efficacy of various forms of thermal insulation in the annular space between the outer surface of the heater and the inner surface of the walls of the converter. Some of the earlier of these experiments were made with a converter similar to those already described but of small dimensions, namely length 3 ft. 6 in. and internal diameter 6 in. The walls were 1 in. thick, the flanges $2\frac{1}{2}$ in. thick and the end-covers $2\frac{1}{4}$ in. thick. The diameter of the catalyst chamber was 3 in. The results of some experiments made in this smaller converter are given in table 2.

Table 2

Experiment	Temperature (°C.) at				Power required (kW.)
	centre of catalyst chamber	top cover outside	middle of converter outside	bottom cover outside	
(a) Reflector tubes unpolished. Air at atmospheric pressure	440	64	104	60	1.01
(b) Reflector tubes chromium-plated and polished. Air at atmospheric pressure	456	57	74	53	0.75
(c) As in (b) but with hydrogen at atmospheric pressure	452	78	140	68	1.61
(d) As in (c) but with hydrogen at 200 atmospheres	440	192	220	122	4.57
(e) As in (d) but with aluminium foil and asbestos paper between inner and outer reflectors	474	188	220	128	4.30
(f) As in (e) but with aluminium foil and asbestos paper in space between outer reflector and converter wall in addition. Process run with hydrogen contaminated with hydrocarbon vapours	500	139	155	143	3.25
(g) As in (f) but with extra asbestos in outer annulus	490	126	150	141	2.81

In experiment (a) the annular space surrounding the catalyst chamber contained two concentric steel cylinders which served as reflecting tubes to reduce the loss of heat by radiation and convection. Experiments (a) and (b) show the reduction in power-consumption and surface temperature due to decrease in the transfer of heat by radiation brought about by the chromium-plating of the reflector tubes.

Experiments (b) and (c) show the effect of replacing the air by hydrogen at atmospheric pressure and the resulting increase in surface temperature and power-consumption due to the increased conduction and convection. Experiments (e) and (d) show the enormous effect of the greatly increased convection due to increasing the pressure of the hydrogen.

A consideration of these experiments led to the conclusion that the major part of the heat-loss was due to internal convection. It can be shown that to reduce convection to negligible proportions the size of the gas-filled interspaces in an insulator when these are filled with hydrogen at a pressure of 200 atmospheres must be very much smaller than when they are filled with air at atmospheric pressure. As the dimensions necessary are very much smaller than can be obtained in practice by increasing the number of reflector tubes, it was decided to fill the space between the two reflector tubes with alternate layers of aluminium foil and asbestos paper, free spaces in this zone being thus reduced to negligible dimensions. The aluminium foil is impervious and acts moreover as an additional reflector and yet is so thin that the increased conductivity is small. That the whole available space was not filled in this experiment was a compromise, as at this stage it was desired to preheat the hydrogen by making it traverse the insulation space before entering the catalyst chamber. The result of this packing is shown in experiment (e) which may be compared with experiment (d). At first sight the improvement appears slight, but in this experiment it must be noted that the temperature in the catalyst chamber was 474°C , as compared with 440°C , and the saving in power was in reality more than that shown.

At a later stage when the attempt to preheat the hydrogen by this method had been abandoned, the space between the outer reflector tube and the converter wall was also packed with asbestos and aluminium foil, and a process run, in which tar and hydrogen were treated, was carried out. In this apparatus the reaction products were discharged through a perforated plate at the end of the catalyst chamber into an open cup, from which they were conducted by a pipe through the bottom end-cover of the converter. The annular insulation space was thus accessible to the gaseous reaction products. The marked improvement shown by experiment (f) was therefore due in part to the fact that the insulation space contained a mixture of hydrogen with hydrocarbons of lower conductivity. The importance of restricting convection is again shown, however, in experiment (g) in which an improved packing of the thermal insulation material resulted in a further reduction of power.

At a later stage further process experiments were carried out in the larger converter of the type already described on p. 342. The internal arrangement of this was again such as to allow the products free access to the insulation space. The results of the experiments are recorded in table 3.

In experiment (1) reflector tubes were used but the spaces between them were closely packed with asbestos board. In experiment (2) the reflector tubes and asbestos were removed entirely, and in experiment (3) the asbestos board of experiment (1) was replaced by tightly packed asbestos paper. The results of these three experiments thus give an idea of the efficiency of the thermal insulation. The difference

between the results of experiments (1) and (3) was due to the difficulty of packing the asbestos board which gave rise to the formation of gaps between the layers of the insulation material, and thus to increased convection and consequent heat-transfer loss.

Table 3

Experiment and details of thermal insulation. Pressure, 200 atmospheres	Temperature (°C.) at						Power re-quired (kW.)
	centre of catalyst chamber	surface of converter					
		top		centre wall	bottom		
		cover	wall		cover	wall	
(1) Reflector tubes and asbestos board insulation. Hydrogen and hydrocarbons in insulation space	450	134	240	168	98	—	3.4
(2) No reflector tubes or lagging. Hydrogen and hydrocarbons in insulation space	320	116	186	208	100	—	4.4
(3) Reflector tubes restored and packed with asbestos paper. Hydrogen and hydrocarbons in insulation space	500	—	92	114	—	102	1.7
(4) (a) Magnesia and asbestos lagging instead of reflector tubes and asbestos paper. Pure hydrogen in insulation space. Non-process experiment	450	—	178	92	—	132	2.6
(b) As at 4 (a) with hydrogen and hydrocarbons in insulation space. Process experiment	480	—	107	96	—	96	1.6

In experiment (4) the reflector tubes and asbestos paper were not used, and a heater made up similarly to an ordinary laboratory furnace was tried. Magnesia and asbestos packing was placed closely round the heater tube and retained in position by an outer casing which slid easily inside the converter, the small space between them being filled with asbestos paper. The shrinkage of the packing on drying necessitated a few preliminary heating runs after which the spaces formed were repacked.

Two experiments were made with this arrangement: 4(a) was a static run in which tar was not treated and 4(b) was a process run. The results show that there is very little to choose between this form of lagging and that used in experiment (3); they also indicate the greater thermal insulation value of gaseous hydrocarbons as compared with hydrogen.

The possibility of reducing heat-loss by using other gases in the thermal insulation space was also considered. Different gases in the same space and between the same temperature-limits at the same pressure will have different coefficients of convection heat-transfer which will not necessarily be in the same relative order as the conductivity coefficients. Approximate values can be found for relative convec-

tion heat-transfer at atmospheric pressures by the methods described by Fishenden and Saunders⁽³⁾. These data can also be used approximately for pressure-changes by using the indices obtained by Petavel⁽³⁾, p. 109). By this method of calculation the relative values for heat-transfer by convection at a mean temperature of 260° C. and a pressure of 200 atmospheres were found to be much the same for hydrogen and nitrogen but considerably greater for carbon dioxide. The conductivities of these gases, on the other hand, at 260° C. are in the ratios 14 : 2.1 : 1.7 which are theoretically independent of pressure. Thus nitrogen and carbon dioxide have each a low conductivity while the conductivity of hydrogen is seven or eight times as great. If, therefore, convection could be excluded or reduced to a negligible amount, it would be worth while, if possible, to substitute for hydrogen in the insulation space some other gas of lower conductivity such as carbon dioxide or nitrogen, and so reduce the chief remaining source of heat-loss.

The thermal insulation value of different gases was tested in one of the converters of the larger type already described; the thermal insulation consisted of the reflector tubes and tightly packed asbestos paper. The experiments were made in the absence of the process, i.e. tar and hydrogen were not treated.

Carbon dioxide, having the lowest conductivity of the gases mentioned, was tested first. As there was no suitable pump available for transferring carbon dioxide to the converter at a pressure of 200 atmospheres, some preliminary experiments were conducted, (1) at atmospheric pressure and (2) at the maximum pressure obtainable with carbon dioxide from a cylinder. This pressure, at 450° C., was found to be 68 atmospheres.

Table 4

Gas	Pres- sure (atm.)	Internal temperature (°C.) at						
		top	7 in.	14 in.	21 in.	28 in.	35 in.	bottom
H ₂	1	100	322	444	447	456	451	387
H ₂	200	100	444	453	453	467	432	381
CO ₂ 65.8 per cent	1	98	353	449	451	456	450	346
CO ₂ 97.5 per cent	68	151	412	455	453	451	433	350

Gas	Pres- sure (atm.)	Surface temperature (°C.) at			Power (W.) at			
		top	middle	bottom	top	middle	bottom	total
H ₂	1	58	73	60	415	403	338	1156
H ₂	200	109	129	102	586	436	1240	2262
CO ₂ 65.8 per cent	1	38	43	38	272	182	206	660
CO ₂ 97.5 per cent	68	79	58	39	380	272	300 (?)	952 (?)

During the experiments, temperature-explorations were made in the thermocouple pocket in the centre of the catalyst bed, the object being to maintain this at 450° C. as closely as possible. Concurrently the surface temperatures of the outside of the converter and the power necessary on each of the heaters were recorded.

Experiments were made first with hydrogen at atmospheric pressure and at 200 atmospheres, then with carbon dioxide at atmospheric pressure and 68 atmospheres. It must be noted that the gas used in the first of these experiments contained only 65.8 per cent of carbon dioxide at atmospheric pressure, the remaining gas being chiefly carbon monoxide. At 68 atmospheres it contained 97.5 per cent of carbon dioxide; the reason for this is explained later. Table 4 gives the results of these experiments.

From this table it will be seen that the internal temperatures were in all cases maintained at about 450° C. The table shows moreover that the heat supplied and surface temperatures attained with hydrogen at 200 atmospheres were about double the corresponding figures at atmospheric pressure. It is also seen that at atmospheric pressure the impure carbon dioxide required about half the heat input required by hydrogen and gave much lower surface temperatures. The carbon dioxide at 68 atmospheres was better than hydrogen at one atmosphere and it is probable that this improvement would be maintained at 200 atmospheres and a saving of perhaps 40 per cent on power would be obtained. From the thermal point of view, therefore, the results were satisfactory, but difficulties of an entirely different nature, which are discussed later, arose.

Subsequently, four static runs were made to determine the thermal insulation value of nitrogen. The results are given in table 5.

These experiments show that the power requirements with nitrogen in the insulation space are only about 60 per cent of those with hydrogen. In practice, of course, the advantage of using a gas with an increased thermal insulation value would have to be balanced against the expense and complication entailed by the use of an additional gas.

Further experiments with nitrogen and hydrogen in the insulation space were again made with the design of converter (described on p. 343) in which the heater was wound directly on the catalyst chamber. The results recorded in table 6 show the thermal advantage of using this type of apparatus.

Temperature-control. The control of the reaction temperature is rendered difficult by the exothermic nature of the reaction and the relatively poor conductivity of the catalyst support. Heat may be generated more rapidly than it can be dispersed and since the rate of reaction rises with temperature, heat evolution may increase rapidly and cause a hot spot to develop. This excessive temperature leads to the deterioration of the catalyst and possibly to the deposition of carbon and ultimate coking of the catalyst.

Hence it is desirable to know as soon as possible of the presence of any excessive temperature and to take steps to correct it. For this reason, there were usually three thermocouples in the pocket in the centre of the catalyst chamber for indicating the temperature near the top, middle and bottom of the catalyst bed. The thermocouples were movable so that temperature explorations of the catalyst bed could be made from time to time.

The methods of temperature-control tried may be classified under three headings. (1) The use of several separate heaters to control the heat input to the

Table 5

Static experiments	Gas in insulation (per cent)	Temperature (°C.) in catalyst chamber at			Surface temperature (°C.) of converter at				Heater current (A.) at				Total power (kW.)
		top	middle	bottom	top cover	wall			top	middle	bottom		
						top	middle	bottom					
(1)	97 H ₂	467	469	322	83	111	125	92	9.3	10.1	6.5	2.02	
(2)	99.3 N ₂	469	470	320	78	90	78	57	6.1	6.9	7.1	1.23	
(3)	99.3 N ₂	450	450	450	80	94	80	60	6.6	Nil	10.8	1.38	
(4)	95.4 H ₂ 2.5 N ₂	450	451	452	77	108	125	104	9.5	8.0	9.7	2.19	

Table 6

Experiment	Gas	Catalyst temperature (°C.) at			Surface temperature (°C.) at				Heater current (A.) at			Total power (kW.)
		top	middle	bottom	top cover	wall			top	middle	bottom	
						top	middle	bottom				
(1)	H ₂	290	460	460	85	95	100	85	7.5	6.7	7.6	1.27
(2)	N ₂	294	459	478	90	92	58	39	6.5	5.8	4.5	0.77
(3)	N ₂	282	456	482	76	75	52	37	6.0	5.6	4.5	0.70

chamber; (2) preheating of the entering tar and hydrogen before they reached the catalyst; (3) dissipation of the heat from incipient hot spots throughout the catalyst bed by means of metallic heat-conductors.

(1) Experiments with single heaters, whether uniformly wound or with graduated windings, showed them to have insufficient flexibility of control, and the standard system of three separately controlled heaters was soon introduced. It would be anticipated that the end of the catalyst chamber through which the cold tar and hydrogen enter would require most heat, this portion of the chamber serving to heat the materials to reaction point. In the form of heater used in all but the last experiments, however, this was not always the case, for the space between the heater tube and catalyst chamber permitted convection currents to carry the

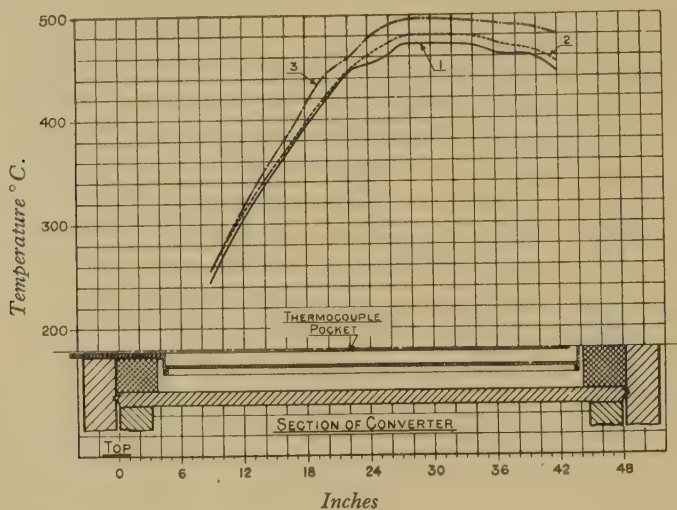


Figure 2.

heat supplied by the lower heaters to the top of the catalyst chamber. In some experiments, in fact, although most of the heat-loss took place at the upper part of the converter, it was found necessary to introduce nearly all the heat at the lowest heater. This is, of course, undesirable from the point of view of control of local heating and also involves running the heater wire at a much higher temperature than would be necessary if the heat were more uniformly distributed—a condition which increases heat-loss and, as will be shown later, is detrimental to the electrical insulation. This difficulty was largely overcome in the apparatus in which the catalyst chamber wound directly with the heating wire was used.

Typical temperature-exploration graphs of the wound catalyst chamber when running with the hydrogen in the insulation space are given in figure 2.

(2) In the catalyst chamber as normally arranged a considerable volume of catalyst near the inlet serves to bring the materials to reaction temperature. If it was attempted to maintain this region of temperatures in the neighbourhood of 450° C. by increasing the power on the corresponding heater, it was found that

coking of the tar usually ensued owing to the fact that the large flow of heat inwards and the poor conductivity of the catalyst bed caused considerable temperature-gradients and consequently excessive temperatures near the periphery of the bed. Attempts were therefore made to preheat the tar and hydrogen to a moderate degree, and with a smaller temperature-gradient, before they entered the catalyst bed.

A preheater at the upper end of the catalyst chamber was therefore designed and is shown in figure 3. This consisted of a cylindrical block of mild steel 8 in. long and 3 in. in diameter made so as to fit very tightly into the top of the reaction chamber. For the passage of the tar and hydrogen a U-shaped spiral groove $\frac{3}{16}$ in. deep and $\frac{3}{16}$ in. wide was cut in the surface of the block, the pitch being $\frac{1}{4}$ in. and the total length 25 ft. The tar and hydrogen passed via an internal channel to the beginning of the groove and similarly were led to the centre of the catalyst chamber at the other end. The top of this block was welded to the top of the catalyst chamber.

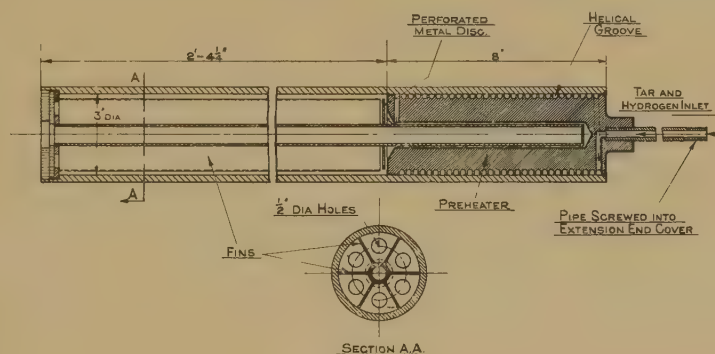


Figure 3.

During the first run with this arrangement, difficulties were experienced with excessive pressure-differences between the inlet and outlet of the spiral, and it was found that the spiral groove became filled with coke.

The spiral groove in the preheater was accordingly enlarged so as to be $\frac{7}{16}$ in. deep and $\frac{7}{16}$ in. wide with a pitch of $\frac{1}{2}$ in. and a total length of 12 ft. A few more or less satisfactory runs followed, in which pressure-differences were only noticed during the first few hours (i.e. while the plant was warming up). The experiments, however, were rather inconclusive as to the utility of this form of preheating although the indications were that this metal preheater offered no advantages over the catalyst bed.

Further experiments were made at a later stage. The catalyst chamber was extended by 2 in. and the top 7 in. of the chamber were filled with (i) pressed steel turnings and (ii) compressed steel wool. With these arrangements good temperature-control and temperature-distribution were obtained.

All experiments on temperature-control were subject to one peculiar difficulty; they were complicated by the fact that the skill of the operators played a large part, and much improvement in control as experiments proceeded was certainly due to the

increased skill of the operators. On the whole the results of the experiments with an internal metal preheater were not such as to justify its inclusion in the final form of apparatus.

(3) In order to disperse the heat arising from hot spots, the effect of placing good metallic conductors in the catalyst bed was tried. These took the form of six mild-steel strips of the same length as the catalyst chamber. These were disposed radially, and as far as possible were in contact with the outer wall. It was considered that this arrangement showed an improvement in ease of control and elimination of hot spots, and it was determined to carry the principle further to arrive at a more definite conclusion.

A new catalyst chamber shown in section in figure 4 was therefore constructed; it consisted of a mild steel cylinder 3 ft. 3 in. long and $3\frac{1}{2}$ in. in external diameter. Round the circumference were bored five longitudinal holes $\frac{1}{8}$ in. in diameter to contain the catalyst and one central hole to accommodate the thermocouple pocket.

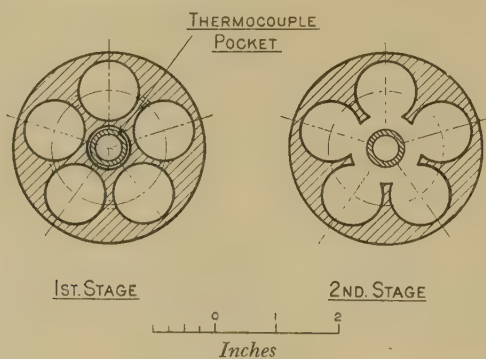


Figure 4.

The top of the cylinder was cup-shaped in order to facilitate the equal distribution of tar and hydrogen among the five tubes of catalyst. With the same end in view, horizontal holes were bored near the top of the tubes to provide intercommunication between them. The rate of flow of tar and hydrogen were reduced proportionately to the reduced amount of catalyst present.

The first run with this arrangement was difficult to control and on examination it was found that all the tubes had coked up over considerable portions of their length. It was concluded that there had been higher temperatures in the tubes than had been measured in the thermocouple pocket and that the tar-distribution between them had been irregular.

To minimize these difficulties the hole for the thermocouple pocket was bored out to a diameter of $1\frac{1}{8}$ in. so that it cut into the holes for the catalyst throughout its length, thus affording communication between them and yet leaving sufficient metal to improve the conductivity. The thermocouple pocket was fitted in position and the space around was filled with catalyst. A run lasting seven days was made with this chamber, during which there was little difficulty in control and little trouble from hot spots. Temperature-explorations showed that a large part of the

catalyst bed was at a uniform reaction temperature. This experiment proved that the increased metallic conduction provided had been of real value and confirmed the conclusion drawn from experiments with metallic strips.

The occupation of space by metallic conductors reduces the volume of catalyst and so reduces the throughput of raw material, and it becomes a matter of judgment how far it is worth while to carry the principle of improving conductivity in this way. In this connexion it must be borne in mind that with a grain-size of catalyst-support of about $\frac{1}{8}$ to $\frac{1}{4}$ in. the interspaces are so large that under the conditions of high pressure and considerable temperature-gradient the convection is probably more important than the conduction of heat. This has been shown in connexion with the experiments on thermal lagging. The introduction of metallic conductors, although improving conduction, may to some extent restrict lateral convection currents, and it is perhaps due to this that the advantage of using the fins was not as great as had been anticipated. To improve the dissemination of heat by convection would involve using large grain-sizes. This, however, is undesirable as the catalyst in larger grain-sizes deteriorates more rapidly.

§ 4. PROBLEMS RELATING TO ELECTRICAL INSULATION

From the electrical point of view the chief difficulty encountered was the maintenance of electrical insulation between the heating elements and earth, and between the coils of the heating elements. Difficulties were materially increased by the fact that the only source of power available was a 220-V. d.-c. supply. There is no doubt that one of lower voltage and isolated from other plant would have been an advantage.

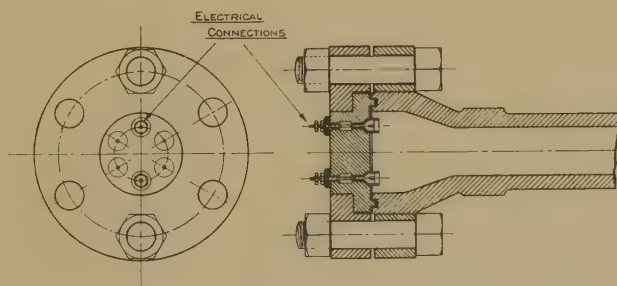


Figure 5.

The electrodes carrying the currents were brought into the converter through the cover by steel rods which passed through conical red fibre bushes as shown in figure 5. Red fibre has so far shown itself to be the most satisfactory substance for this purpose and can be used up to temperatures of 150°C . Most other substances are too rigid or too plastic at such high temperatures to remain tight at a pressure of 200 atmospheres, but other materials have been and are being investigated with a view to their substitution in certain cases. Inside the converter the steel rods were encased in silica or pyrex glass tubes surrounded by asbestos packing. In the earlier

experiments, when the wall temperature of the converter was high, extension pockets which could be water-cooled and whose ends carried the red fibre joints were used. Trouble was, however, experienced owing to the condensation of moisture on the terminals. A diagram of one of these extension pockets is shown in figure 5.

In the first experiments the elements of the heater were wound on a silica tube. This, however, was usually found cracked and broken after two or three runs, and on one occasion was disintegrated into small fragments which were found to be slightly explosive, a property they retained for over a year. The phenomenon was evidently due to the occlusion of hydrogen in the silica at high temperatures and pressures, the permeability of silica to gases increasing rapidly at high temperatures.

The heating elements were thereafter wound on an iron tube and insulation was effected by means of a layer of mica held between two sheets of asbestos paper on the outer of which the wire was wound. The spaces between the turns of wire was usually filled with a fireclay cement.

In the first form of apparatus an attempt was made to preheat the hydrogen before it joined the tar by circulating it through the thermal insulation space. With this apparatus trouble was experienced in maintaining the electrical insulation, and certain mechanical difficulties arose; this attempt to preheat the hydrogen was accordingly abandoned and simpler forms of apparatus such as those already described were adopted. It was found very difficult, however, to maintain the electrical insulation owing to the deposition of moisture on the electrodes inside the converter. This moisture was derived by distillation of hygroscopic moisture from the hotter parts of the asbestos lagging and from asbestos, such as that under the heater, raised to 600°C. , at which temperature water of constitution is given off to the extent of about 15 per cent. In those experiments in which the products of reaction had access to the insulation space the trouble was greater, as water is one of the products of reaction. It must be noted that, at the high pressures used, water will distil from the hotter regions to the colder and deposit there in liquid form at all temperatures below its critical temperature, and as the electrodes, on account of the red fibre bushes, were kept as cool as possible they received this condensation very markedly. This was noted in the first few experiments made with the converter with an extension pocket; the trouble was eventually greatly reduced in that form of construction by filling the pocket with a high-melting-point bitumen. Later, when it was found possible to insert the electrodes directly through the lower cover of the converter, the trouble again became acute as the water collected in the bottom. The insulation was again restored by making wider holes on the inside surface of the cover where the electrodes passed through it (the fibre bush being at the bottom of the holes) and filling them with a non-volatile hydrogenated tar oil whose density was greater than that of water up to 100°C. These methods, while effective within limits, were only palliations. A more direct method was to dry out the lagging before each run by heating up the converter and exhausting the insulation space containing the lagging. The amount of water abstracted in this way was remarkably high and the insulation obtained was good. In these experiments, however, in which the products of reaction had access to the insulation space, the

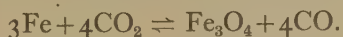
electrical insulation would again gradually fall until it was only a few thousand ohms. When this space was swept out by means of pure dry hydrogen, and so re-evaporating the water formed, the insulation was usually restored to some extent. In the later forms of construction, where the catalyst chamber was not in connexion with the insulation space and the latter was filled with hydrogen or nitrogen, trouble due to the deposition of moisture was eliminated if the converter was dried out *in vacuo* before the run.

As regards the insulation of the heating element itself, moisture could not be deposited, the temperature being too high. The first trouble with the heater occurred through deposition of carbon on its surface and in the insulation material under and between the wires. This occurred sometimes in runs in which the hydrocarbon vapours from the reaction had access to the insulation space, when, if the temperature of the wire was high, cracking of some of these vapours would ensue in spite of the excess of hydrogen. This was markedly shown in some experiments in which the top heaters, which were hottest, became earthed owing to carbon deposit. This form of trouble was also eliminated when designs were adopted in which the outer space was filled with pure nitrogen or hydrogen.

During experiments for determining the thermal insulating properties of different gases, a similar difficulty in maintaining electrical insulation was experienced when carbon dioxide was used. This difficulty, which led to the abandonment of carbon dioxide, is perhaps of sufficient interest to be described at some length.

The heater and insulation material used in the experiments were new and uncontaminated, although the catalyst chamber had been used previously and was coated with a film of ferrous sulphide. The converter was first dried out by heating *in vacuo*, and then the experiments with hydrogen were carried out. The converter was again evacuated, and the experiments with carbon dioxide were carried out. During these experiments, insulation trouble developed and in the last experiment with carbon dioxide at high pressure the insulation of all heaters decreased seriously. The line conductivity of the lower element greatly increased, allowing a large current to flow and making the power-measurement on this heater uncertain—hence the query in table 4. The carbon dioxide from the cylinder was 98.5-per-cent pure, but when a sample was drawn from the converter during the course of the experiment at atmospheric pressure it was found to have the following composition: CO₂, 66; CO, 28; and H₂, 6 per cent. Repeated experiments gave the same result. In the high-pressure experiments, on the other hand, the purity of the original carbon dioxide had only fallen very slightly from its value of 98.5 per cent after many hours heating.

The explanation of these phenomena is probably given by the following equilibrium:



The presence of carbon monoxide suggested the possibility of iron carbonyl being formed under certain conditions and subsequently decomposed. It is probable that iron carbonyl was formed in the regions where the temperature was most favourable and diffused to the heater, where it was decomposed and iron was

deposited between the turns of the winding and between the winding and tube, leading to partial short-circuiting. On cooling, the iron again largely recombined to form iron carbonyl and the insulation improved. This would also explain the observed increase of insulation and of conductivity resistance which took place when the heater cooled.

This explanation was confirmed after the experiment when iron was found in the insulating material in the neighbourhood of the wire of the heater. Some Fe_3O_4 was also found on the surface of the catalyst chamber after these runs. It is probable that the hydrogen found was desorbed from the steel which had been subjected to high hydrogen-pressure.

For all early experiments the heater tube itself had not been insulated from the converter; in later experiments a great improvement in the insulation of the heaters from earth was effected by interposing a block of sindanyo between the tube and the legs connecting it to the converter. This was found to increase the electrical insulation from 40 M Ω . at room-temperature and 3 M Ω . at 450° C. to nearly double these values. By this means it was found possible to make long runs in which the insulation was maintained at values of the order of 100,000 Ω ., but it was found that there were other factors the consideration of which could lead to further improvement.

It had been noted on many occasions that rise of temperature of the heaters was accompanied by a great fall in electrical insulation, whatever the pressure of the gas in the thermal insulation space. This might be of the order, *in vacuo*, of 80 M Ω . at atmospheric temperature to 4 M Ω . at a temperature of 400° C. in the catalyst chamber, which is lower than the running temperature of the wires. If an abnormally high current was carried by one of the elements, still lower values were obtained.

This result was at first attributed entirely to the rapid decline in insulating power of such materials as mica and asbestos as they are raised in temperature, and there is no doubt that this was largely the cause. There were, however, other observations to show that a further cause was probably operating. Apart from the temperature effects above referred to, the observations were that insulation (*a*) was not so good *in vacuo* as when a gas was present; (*b*) was not so good in hydrogen as in nitrogen or air; (*c*) was not so good at low as at high pressures. These observations led to the conclusion that it was probable that thermionic emission from the heater wires was at least partly responsible for the fall of insulation, as a comparison with the known facts concerning thermionic emission shows. Thus, emission increases very rapidly with rise of temperature, and is greater when the emitter contains occluded gas. In addition, ionic mobilities are greater *in vacuo* and in gas at low pressures than in gas at high pressures, and are greater in hydrogen than in nitrogen.

In the design of the last arrangement, in which the heating wire was wound directly on the catalyst chamber, the latter could not be insulated from the rest of the converter. The thickness of the mica insulation on which the heaters were wound was therefore increased from $\frac{1}{32}$ to $\frac{1}{16}$ in. to compensate in some degree for this. In the runs with this converter, it has already been shown that owing to the direct application of the heat (*a*) the currents were small and the temperatures

of the wires lower than usual and (b) no wire carried an excessive proportion of current. The result of this was that the best values of electrical insulation maintained during a continuous experiment were secured. The insulation of the system started at 100 MΩ. at atmospheric temperature and was found under running conditions not to fall below 0.25 MΩ. with hydrogen or 2.0 MΩ. with nitrogen.

§ 5. ACKNOWLEDGMENTS

The authors wish to thank the Director of Fuel Research, Dr F. S. Sinnatt, for his permission to publish this account, and to their colleagues on the staff of the Fuel Research Station for their collaboration at all stages of the work.

REFERENCES

- (1) *Fuel Research Tech. Paper*, No. 41 (1935). H.M. Stationery Office.
- (2) BARBER and TAYLOR. *Proc. Instn. mech. Engrs*, Lond., **128**, 5 (1934).
- (3) FISHENDEN and SAUNDERS. *The Calculation of Heat Transfer*, Chap. VII and Appendix C.

THE BEHAVIOUR OF A SINGLE-HAIR HYGROMETER UNDER VARYING CONDITIONS OF TEMPERATURE AND HUMIDITY

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ABSTRACT. A sensitive single-hair hygrometer is described which enables observations to be carried out, over an extended range, on the effects due to variations in relative humidity and in temperature. The temperature coefficient of a stretched hair in an atmosphere kept at a relative humidity of 100 per cent is negative for temperatures above about 1.5°C . and positive in the range below that temperature. If the hygrometer is kept at a constant temperature and the relative humidity of the air is decreased from 100 per cent there is an immediate increase in length, corresponding to an apparent increase in relative humidity of about 3 per cent, followed by a contraction to the equilibrium length characteristic of the lower humidity. It seems probable that this effect may account for the apparent supersaturation sometimes seen in balloon meteorograph records. With this hygrometer the scale value for relative humidity was dependent on temperature. The lag in response of the single hair varied with experimental conditions, and was often considerable. It will have its maximum effect when humidity is varying rapidly as in a rising balloon, but will be of much less importance with hair hygrometers used on the ground, since there conditions alter relatively slowly, and the hair will always be in approximate equilibrium with the air surrounding it.

§ 1. INTRODUCTION

BALLOON meteorograph records obtained with a hair hygrometer⁽¹⁾ appear to indicate in certain cases conditions of supersaturation in the upper atmosphere⁽²⁾. The records shown in figure 1, kindly supplied by Mr Dines, show this effect at 0.7 and 2.7 km. on the ascent and again at 0.9 and 2.2 km. on the descent. As it is difficult to picture the conditions under which supersaturation would occur, we decided to carry out some experiments to ascertain whether the effect could be produced under controlled conditions in an atmosphere at a relative humidity of not more than 100 per cent.

The length of a stretched hair in a moist atmosphere is a measure of the relative humidity of that atmosphere. The equilibrium between hair and atmosphere must be dynamic, as many molecules of water leaving the hair as arrive and are absorbed; equilibrium takes a finite time to be established. There is no experimental evidence to show that a hair can absorb more water than it does in a saturated atmosphere. Actually it is usually assumed by meteorologists that a hair immersed in water

registers a relative humidity of only about 95 per cent, when its length in saturated air is taken to be equivalent to a relative humidity of 100 per cent, though one might perhaps expect an increase in length under these conditions. But the surface conditions are very different for a hair immersed in water and for one in a saturated atmosphere, and it is possible that an increase in the vapour-content of air already saturated would cause the hair to absorb more water molecules and so increase in length. It is also possible that a change in temperature at constant relative humidity

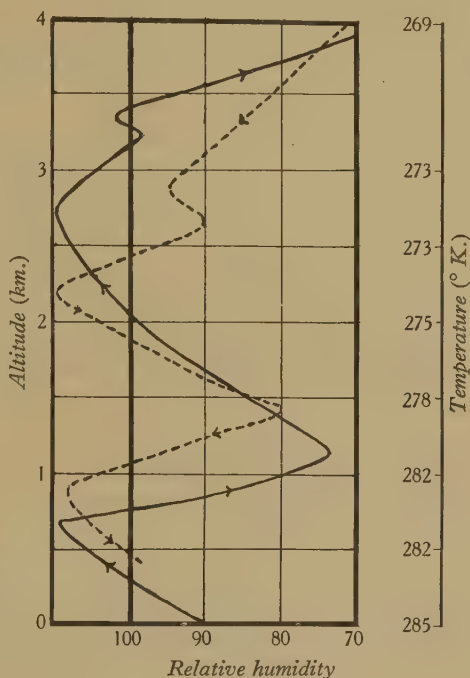


Figure 1. Balloon meteorograph record. The full curve is the record obtained while the balloon was ascending, the dotted curve while descending. The saturation line shown is that obtained by immersing the hair in water. This is usually taken to represent a relative humidity of only about 95 per cent.

might temporarily alter the equilibrium in such a way as, for instance, to decrease the rate of loss of water while maintaining the absorption-rate constant, and so produce an increase in length suggesting supersaturation.

Some rough qualitative experiments made with a recording hair hygrometer kindly lent by the Meteorological Office, and with a single hair hygrometer, showed that a fall in temperature from 15°C. to 0°C. at a constant relative humidity of 100 per cent did, when temperature and length had again reached equilibrium, produce an increase in length. This negative temperature coefficient is in agreement with the results of Griffiths⁽³⁾ and Pfeiffer⁽⁴⁾ but contrary to those obtained by Grundmann⁽⁵⁾.

The experiments also showed that a hair maintained for a considerable time at a relative humidity of 100 per cent developed a certain plasticity, and that its

readings were not quantitatively reproducible. We found that even more irregular behaviour resulted from a complete drying of the hair. In later experiments we were careful, therefore, to avoid leaving the hair for many hours in a very wet or dry atmosphere; for this reason air at room humidity was drawn into the hair-chamber at the end of a day's run.

The human hairs used were prepared by soaking in ether, carbon tetrachloride or alcohol, but the method of preparation had no apparent effect on the behaviour of the hair. Five of the hairs were kindly supplied by Mr Dines, and had been prepared in the same way as those used in the balloon meteorograph. Only one of these hairs (no. 4) received any further treatment; it was soaked in ether for 24 hours, and washed in distilled water before use. The behaviour of this hair was identical with that of the others.

The time required for the hair to reach complete equilibrium when the temperature was varied by about 10° C. was of the order of 1 hour, and a similar lag has been observed by other investigators.* It appears to be impossible to maintain supersaturation in an atmosphere long enough for the hair to attain even approximate equilibrium. Temporary supersaturation can only be attained by processes involving temperature-changes in the air, and as it is desirable to separate the effects due to alterations in relative humidity from those due to temperature we made no attempt to work in a supersaturated atmosphere.

§ 2. APPARATUS

The apparatus adopted was designed to allow measurements of the change in length of the hair with change of relative humidity or of temperature, in stagnant or flowing air. The construction of the hygrometer is shown in figure 2*a*. The hair *H* is mounted on a stainless steel pillar, supported by a stand with three levelling-screws, and carrying at the top a bracket to support a loaded optical lever. The arrangement of the optical lever allowed the maintenance of a sensibly constant tension of 1.5 g. on the hair, permitted the maximum angular deflection to be read, and was easy to adjust for zero. This is the load used in the balloon hygrometers, but is three times as great as that employed in the recent work of Grundmann⁽⁵⁾. The pivot of the mirror was a roller of stainless steel, and worked very smoothly. The movement of the mirror was observed by means of a telescope and scale, combined with a reflecting prism.

The hygrometer was contained in the refrigerating chamber shown in figure 2*b*. This was in the form of a cylindrical tube of internal diameter 7 cm., whose walls were formed by a spiral coil made of copper tubing $\frac{3}{8}$ in. in diameter, wound closely and soldered solid on the outside, to give an airtight vessel with a capacity of about half a litre. This gave very efficient cooling inside the chamber, when cold alcohol was circulated by a gear pump through the spiral, because of the large area of cold metal in contact with the air. The base was formed by a brass disc *A*, to which was soldered a brass tube fitting inside the lower portion of the copper spiral. This was supported on three glass tubes *G*, 1 in. long, and was clamped to a piece of slate *B*

* See for instance Griffiths⁽³⁾.

by brass screws, one passing down the axis of each glass tube. This slate was supported on four pieces of cork, and clamped to the slate bench by a single bolt *C*. This arrangement ensured a rigid support, while providing good thermal insulation when the whole was packed in slag wool. The experimental chamber had an inner base *L*, which supported the hygrometer, and stood above a shallow vessel in which could be placed water, or a solution of known vapour pressure. The presence of

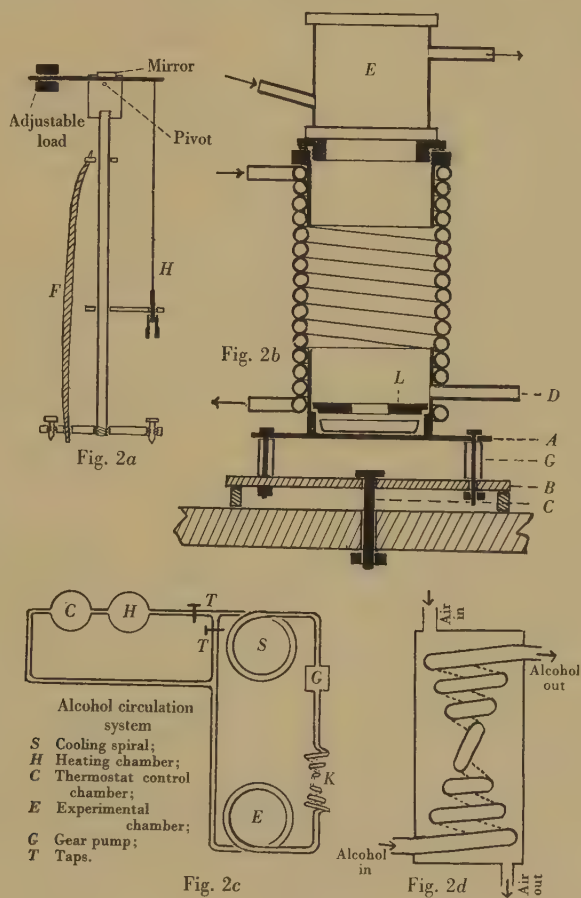


Figure 2.

liquid in stagnant air maintained the relative humidity at a constant value but it took a long time to attain equilibrium in the vessel when the temperature was changed. To aid the establishment of equilibrium a piece of filter paper *F*, figure 2*a*, dipped into the water and was held parallel and close to the hair by two clips on the stainless steel pillar.

This experimental chamber could also be used with flowing air. In this case conditions more closely resemble those in which the balloon records were obtained. Inlet and outlet tubes (not shown in figure 2*a*) were inserted so that air of known humidity could be admitted at the top and flow out through the base. The dish of

liquid placed in the chamber for the stagnant air experiments was, of course, removed.

The mirror of the hygrometer was observed through the top of the cooling-chamber, which was closed by the vessel *E*, made of two parallel glass plates, separated by a jacket through which dry air was circulated. This vessel screwed into the top of the chamber, and an air-tight joint was made by a rubber washer. This arrangement was adopted to prevent the obscuration of the glass by moisture, and proved quite satisfactory.

There were three thermocouples inside the chamber, one in the water, one near the wall of the chamber, and one as near as possible to the centre of the hair, the leads coming out through the tube *D*. It was found that they all showed the same final temperature.

A test was made to determine the deflection of the optical lever due to the contraction of the supporting system which occurred when the temperature of the apparatus was lowered. A phosphor-bronze wire of known expansion coefficient was mounted in place of the hair, under sufficient tension to keep it taut, and allowed to attain a constant length at 15° C. The temperature was then lowered and the change in scale reading was observed when temperature and length again became constant. From these observations the shift of the beam of light due to the change in length of the steel pillar was calculated, and all graphs are corrected for this effect.

The experimental chamber could be maintained at a low temperature by pumping through the tubular wall alcohol cooled by circulation through a spiral tube kept at a constant temperature in ice or solid carbon dioxide. It was hoped that it would be possible to produce any desired temperature in the chamber by controlling the speed of circulation. However, the thermal insulation proved so efficient that any alteration in the speed of pumping merely changed the rate of fall of temperature, and not its final value. Since it was obviously necessary to have the whole system well lagged in order to maintain a steady temperature, independent of room temperature fluctuations and draughts, over long periods, the control of temperature had to be effected by reheating the cooled alcohol to any desired extent before circulating it round the vessel. For this purpose the alcohol was passed in turn through the cooling spiral *S*, figure 2*c*, kept at a constant temperature, a heating-coil chamber *H*, a thermostat control chamber *C*, the experimental chamber *E*, a coil *K* to be described later, a gear pump *G*, and back to the cooling spiral.

The thermostat operated a hot-wire mercury-switch relay in a circuit containing a two-way switch. In one position the two-way switch allowed current to pass continuously through one half of the heating-coil, which was centre-tapped, and through the other half when the thermostat control permitted. In the other position the current was completely controlled by the thermostat.

The gear-pump casing was made of ebonite, in order to provide good thermal insulation. The pump was driven through a reduction worm and pinion gear of about 56 to 1. The pump and motor were mounted on a heavy iron pillar which rested on four pieces of soft rubber; this gave satisfactory insulation against any

mechanical vibration which might have been transmitted through the block floor and bench to the optical lever. The speed of the motor could be controlled, and was measured by the reading of a suitably calibrated ammeter.

To produce a steady flow of air at any desired relative humidity the humidity-controller of Walker and Ernst was used⁽⁶⁾. In this apparatus a blower produces two streams of air, one of which bubbles through water at a known temperature and becomes saturated, while the other passes over various dehydrating agents. The wet and dry air-streams pass through separate flow-meters, and hence to a vessel where they mix in the proportions indicated by the flow-meters; the mixture is admitted to the apparatus through a third flow-meter.

It was found that, in the arrangement of Walker and Ernst, condensation occurred in the tubes by which the saturated air, which was originally above room temperature, reached the mixing vessel, and hence the relative humidity of the mixture was less than the calculated value. Lagging these tubes was found unsatisfactory. The apparatus was therefore rearranged so that the whole of the path of the wet air and the mixing vessel were contained in the same thermostat as the vessel in which the air became saturated. Although accuracy greater than ± 5 per cent is not claimed, at relative humidities less than 100 per cent, it was always possible to produce a flow of air accurately known to be at a relative humidity of 100 per cent, as the temperature of the thermostat was higher than that of the experimental chamber.

To achieve temperature equality between the hygrometer and the inflowing air, a brass cylinder *K*, figure 2*d*, containing a copper spiral in the form of a double cone, was packed near the experimental chamber, and the cold alcohol circulating round the walls of the latter was passed through this spiral. Air at a known relative humidity and at the temperature of the thermostat entered the cylinder, passed over this spiral cooling-coil, and so attained the temperature of the experimental vessel before reaching the hygrometer. The rate of flow of air through the hygrometer vessel was about 1 litre/min. Tests showed that this temperature-equalization of experimental chamber and inflowing air was perfectly satisfactory, and a knowledge of the initial relative humidity of the inflow and its initial and final temperatures allowed the relative humidity of the air reaching the hygrometer to be calculated.

§ 3. RESULTS

Using the apparatus described we have measured the variations in length of the hairs under the following conditions. (i) Relative humidity maintained at 100 per cent, temperature lowered quickly, with stagnant and flowing air; (ii) relative humidity maintained at 78 per cent and at 88 per cent, temperature lowered quickly, with stagnant air only; (iii) temperature kept constant, relative humidity decreased quickly from 100 per cent, with flow method only; (iv) temperature kept constant, relative humidity decreased quickly from a value less than 100 per cent, with flow method only; (v) we have also measured the percentage change in length due to a known variation in relative humidity for a series of temperatures by the flow method.

With the exception of (ii) each of the above experiments was made with two or

three different hairs, and the hairs were prepared by different methods. In all cases the behaviour was identical, although numerical agreement was not obtained.

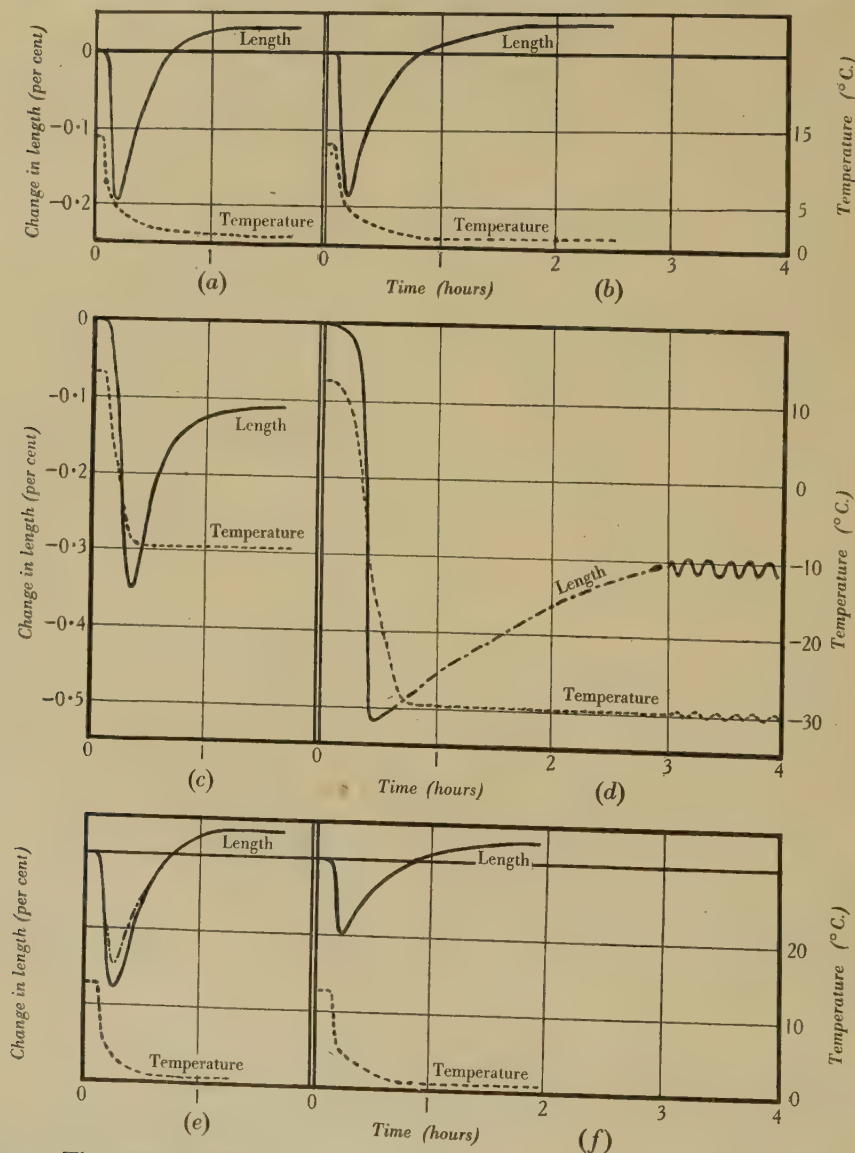


Figure 3. The relative humidity is 100 per cent for (a), (b), (c), (d), (e) and 78 per cent for (f). The stagnant method was used for (b) and (d) and the flow method for (a), (c) and (e).

Typical graphs for case (i) are given in figure 3, the dotted line showing the temperature-change with time.

Both the stagnant and flow methods gave similar results as the hair cooled, but its equilibrium length was rather more quickly attained in the latter method. In all cases the immediate effect of a fall in temperature was a *decrease* in length of the

hair, a minimum length being reached before the thermocouple in the hygrometer chamber became steady. The time required to attain temperature-equilibrium was from 20 to 45 min., though by far the greater part of the fall in temperature had in all cases occurred in 10 min. After this preliminary contraction the hair expanded, reaching a final equilibrium length after from 1 to 3 hours, though most of the change in length had occurred by the end of half an hour.

This initial rapid contraction of the hair appears to be due to experimental conditions. The sudden cooling of the wall of the vessel lowers the water-vapour pressure near it, and the pressure-gradient so set up causes vapour to diffuse out from the centre. There will therefore be an immediate drop in relative humidity near the hair corresponding to its initial rapid response. Temperature-equilibrium on the other hand takes some time to be established, and it is possible to estimate the relative speeds of the two effects. A rough calculation shows that temperature-equalization will occur considerably later than the disappearance of the vapour-pressure gradient.

The hair has completed its contraction and commenced to expand after about 6 min., and by this time the vapour pressure should be uniform throughout the vessel. Owing to the normal lag in response of the hair the final length will not be attained for about an hour, and by this time temperature-equilibrium is achieved.

The fluctuations appearing in the temperature line of figure 3*d* support this explanation. The variations are about 1° C. and are due to the switching on and off of the heating-current owing to unsatisfactory setting of the thermostat contacts. The other curve in figure 3*d* shows variations in the length of the hair of about 0.01 per cent, approximately synchronizing with the temperature variations. Two or three curves of this nature were obtained. In the case of flowing air there were some irregularities in the fluctuations of temperature and therefore of length. Hence it was possible to distinguish corresponding peaks in the temperature and length graphs, and it was found that the length-variation lagged behind the temperature-change by about 4 min.

Figures 3*a*, 3*b*, 3*e* and 3*f* all show a final length greater than the initial, while in figures 3*c* and 3*d* the hair is shorter than at the commencement. In figure 3*d* the rise to the final steady value is indicated by a dotted line, since the points on the ascending portion of the graph were scattered owing to the fluctuations of temperature mentioned above. These occurred throughout the run, after the initial sudden temperature-drop, but are only indicated on the figure during the equilibrium period of the hair.

It was thought that the initial drop in relative humidity near the hair was assisted by the presence of dust acting as condensation nuclei. A filter consisting of a glass tube 12 in. long, $2\frac{1}{2}$ in. in diameter, and packed with wool, was inserted in the air circuit to remove dust. Since the wool was hygroscopic the filter had to be placed in the air intake, and so did not remove any drops carried in the airflow. The result, shown in a broken line in figure 3*e*, was a decrease in the amount of the initial contraction, probably due to the reduction in the number of condensation nuclei by the removal of dust.

Expansion coefficient. Figure 3 shows that the final length of a stretched hair cooled from room-temperature may be either greater or less than its original value, the equilibrium length attained depending only on the final temperature. In figure 4 are shown the results of cooling the same hair in a saturated atmosphere to several final temperatures. The change in length of the hair is expressed as a percentage of its length at the initial temperature of 16°C. and is plotted against the final steady temperature attained. In all cases the hair was in equilibrium with the moist air before cooling commenced, and was left long enough to attain a constant length after cooling. We found that the final length attained by the hair was a true equilibrium value since it was the same whether it was cooled from, say, room-temperature to -10°C. , or cooled from room-temperature to 0°C. , allowed to reach equilibrium at 0°C. , and then cooled to -10°C.

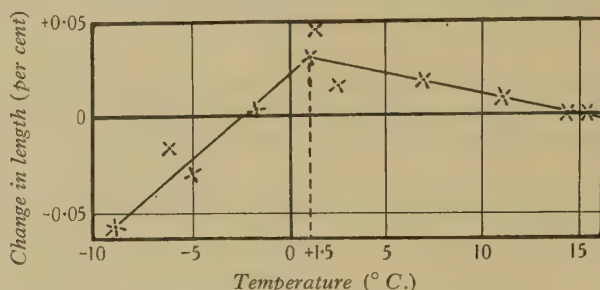


Figure 4. Variation of length of hair with temperature when relative humidity is 100 per cent.

The coefficient of expansion of a hair in a saturated atmosphere changes sign at about 1.5°C. It is negative for the range from 20°C. down to 1.5°C. , but for temperatures lower than 1.5°C. it has a positive value, so that a hair maintained at a relative humidity of 100 per cent and initially at 1.5°C. will show a final decrease in length when either heated or cooled.

The coefficients of expansion on either side of 1.5°C. are approximately constant over the range investigated. Down to 1.5°C. the values obtained for two typical hairs were -2.3×10^{-5} and -1.9×10^{-5} , and for lower temperatures $+9.9 \times 10^{-5}$ and $+14.6 \times 10^{-5}$ per unit length per $^{\circ}\text{C.}$ Figure 4 shows that the hair, no. 5, cooled from 16°C. attained its original length at -3°C. , but the temperatures at which the lengths are the same will vary from hair to hair owing to variations in temperature coefficient.

The temperature at which the length is a maximum cannot be fixed with precision though it seems to be the same within 1 or 2°C. for all hairs investigated, and to be above 0°C. It is possible that at the inversion temperature some change of state of the absorbed water occurs with change in its vapour pressure and in its actual volume. It is difficult to say what would be the freezing-point of the absorbed water.

These results account for the discrepancies in expansion coefficient obtained by various observers and referred to above; for the value obtained will vary with the temperature-limits if the temperature-range passes through 1.5°C.

We conclude that temperature-variation will have only a small effect on the balloon hygrometer records, for the instrument will in this case be moving rapidly through a temperature-gradient, and through layers of varying relative humidity. Though it will not have time to reach equilibrium in any particular layer, its reading will, unless the relative humidity varies very considerably, approximate to the correct relative humidity for the corresponding height recorded by the barograph. There will be no deflection corresponding to the initial decrease in length observed in our experiments, since there will be no conditions occurring which correspond to those

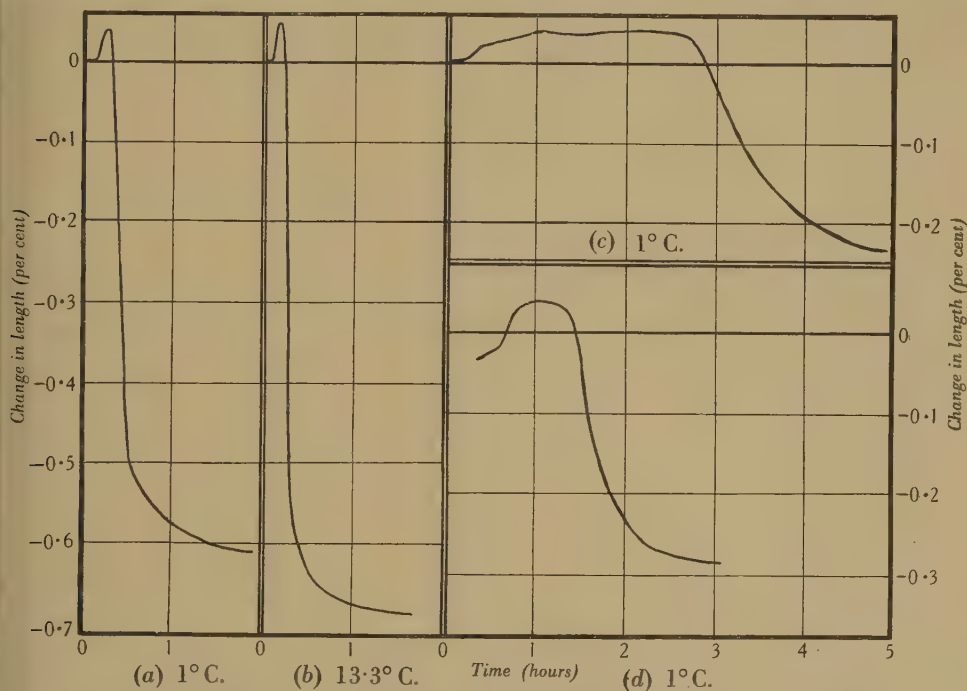


Figure 5. Apparent supersaturations produced on lowering the relative humidity from 100 per cent.

causing the vapour pressure gradient in the experimental chamber. The correction due to the temperature coefficient will probably be small compared with the error due to the lag of the instrument.

In case (ii) the relative humidity was constant at 78 and 88 per cent and the temperature was lowered quickly. A saturated solution of sodium or of potassium chloride was placed in the dish in the hygrometer vessel, so that the relative humidity of the stagnant air above it was maintained at the corresponding maximum vapour pressures of 78 and 88 per cent respectively. The saturation vapour pressure of these solutions varies only about 2 per cent over the range of temperature 12° to 0° C., and thus it was possible to observe the effect of change of temperature when the relative humidity was maintained approximately constant at a value less than 100 per cent. The initial result of lowering the temperature was, as at a relative humidity of 100 per cent, an immediate contraction of the hair, figure 3f. It

therefore appears that a drop in relative humidity due to the vapour-pressure gradient occurs in this case also. The temperature coefficient at these lower humidities had the same sign and approximately the same value as at a relative humidity of 100 per cent, though the investigation was not in this case carried below 0° C.

(iii) In the case where the temperature was constant and the relative humidity decreased from 100 per cent the following observations were made.

The apparent supersaturation. Experiments were carried out in the flow apparatus, and in every case the initial result of decreasing the relative humidity from 100 per cent was an immediate increase in the length of the hair, figure 5. This occurred even when the hair had not been in the saturated atmosphere long enough to attain its equilibrium length, figure 5*d*. This apparent supersaturation occurred for all temperatures investigated and its duration was from 10 min. to 3 hours. Observations are given in table 1.

Table 1. Apparent supersaturation observed when relative humidity was decreased suddenly from 100 per cent at a constant temperature

Change in relative humidity (per cent)	Steady temperature (°C.)	Duration of apparent supersaturation	Change in length (per cent)	Reference number of hair
18	12.8	40 m.	0.2	4
34	1	2 h. 40 m.	0.38	4
37	12	40 m.	0.2	4
46	1	1 h. 40 m.	—	3
47	1	1 h. 15 m.	0.25	2
63	12	10 m.	0.45	2
66	1	15 m.	0.4	2
71	1	40 m.	0.1	3
76	1	40 m.	0.2	4

The increase in length produced in this way corresponded to an increase in relative humidity to about 103 per cent. It is impossible that such a degree of supersaturation could even momentarily exist in the experimental chamber as condensation nuclei were present in great numbers, the air flowing into the chamber was subject to only a negligible pressure-drop and there could be no appreciable adiabatic cooling. It appears therefore that it cannot be a true supersaturation of the air that is indicated by this extension.

If water vapour had condensed on the hair, reduction of humidity would cause it to evaporate, thus producing a temporary fall in temperature. In the neighbourhood of 10° C. this would cause an expansion, but an expansion of the observed magnitude would require a cooling due to evaporation of about 10° C. Also the expansion is still observed at a temperature of 1° C. although the temperature coefficient predicts a contraction with fall of temperature. It is therefore difficult to explain the initial expansion in terms of a temperature-drop due to evaporation, although, as will be seen below, the effect is only observed when the initial relative humidity is 100 per cent, and is therefore probably connected with the presence of drops of water on the hair.

It is even more difficult to account for the widely different durations of the apparent supersaturations under similar conditions. The graph in figure 5c shows the longest time for which it was observed. In those cases where the apparent supersaturation lasted a long time the final contraction of the hair to its equilibrium length at the lower humidity was more gradual than when it lasted only about 10 min.

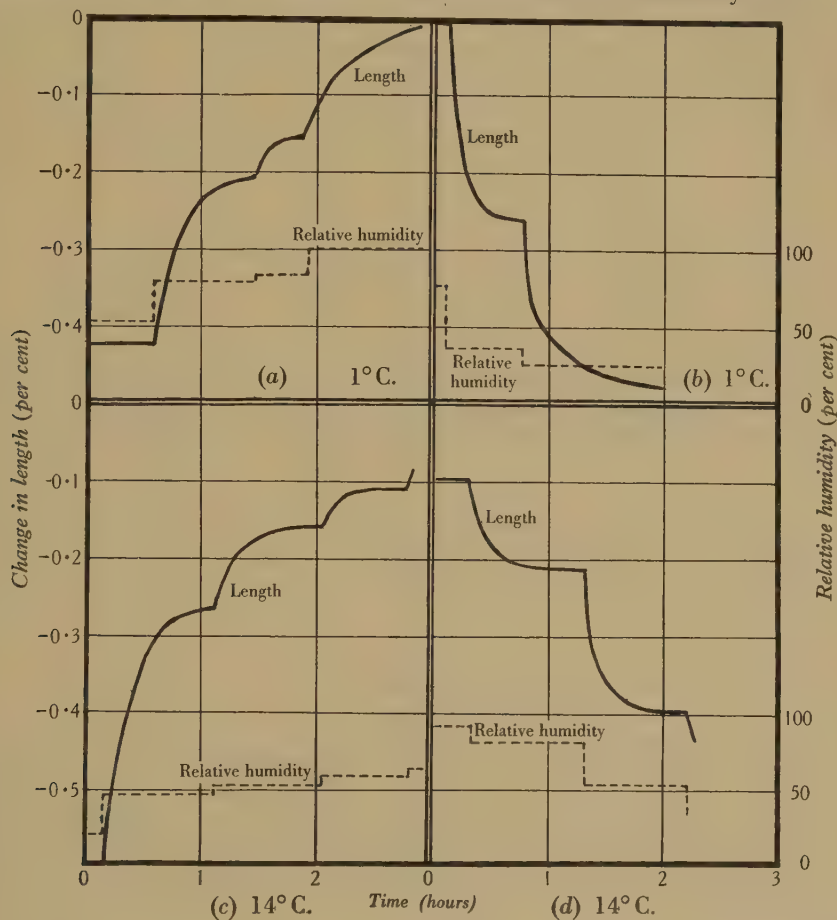


Figure 6.

The initial treatment of the hair does not appear to account for the variation in duration, since two hairs prepared in the same way, and subject to humidity-change at the same temperature, showed supersaturation lasting for 15 min. and 1¼ hours. There are at least two influences acting on the hair, one being the normal loss of water from its cells leading to a contraction, the other connected probably with the evaporation of drops of water from its surface. The latter effect is presumably the more immediate and may account for the fluctuations in length following the switching on and off of the thermostat, as shown in figure 3d.

(iv) When the temperature was constant and the relative humidity varied from values less than 100 per cent, figures 6a to 6d, in every case the length of the hair

followed the change in humidity with a considerable time lag. Equilibrium was reached in times varying from 20 min. to 1 hour, the lag being greater for large changes in humidity. *There was no indication of the initial expansion which occurred when the initial relative humidity was 100 per cent.* The time lag appeared to be about the same at all temperatures for a given drop in humidity.

(v) From curves similar to those discussed under (iii) and (iv), it was possible to determine the length of the hair with respect to its length at 100 per cent for any relative humidity at the temperatures 16° and 1° C. These results are plotted in figure 7.

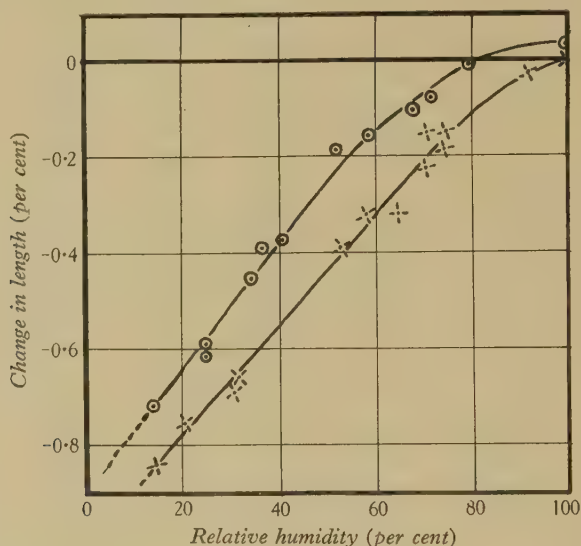


Figure 7. Variation of length with relative humidity. ○ Temperature 0° C.; × Temperature 16° C.

At 100 per cent the hair is only slightly longer at 1° than at 16° C., but the curve for the lower temperature lies always above that for the higher, and at relative humidities of about 50 per cent there is a discrepancy of about 15 per cent in relative humidity between the two curves, showing that a hygrometer calibrated at room-temperature is unsuited for use at the lower temperature.

It is interesting to compare this result with the theory of Sresnevsky quoted by Whipple⁽⁷⁾. He considers the negative pressure Q developed in a cell partially filled with liquid, i.e. the intra-molecular spaces in the hair, and obtains the formula

$$Q = R\rho\theta \log \left(\frac{p_0}{p_1} \right) - P_0,$$

where ρ is the density of the liquid, θ the absolute temperature, p_0 the saturation vapour pressure at temperature θ , p_1 the vapour pressure in the cell, and P_0 atmospheric pressure.

Hence the force causing the hair to contract is proportional to the absolute temperature and inversely proportional to the relative humidity. For a range of temperature down to 1.5° C. the change in length with temperature at constant

relative humidity, which we observed, is in the direction predicted by this theory. The theory however does not agree with experiment at lower temperatures, and there are apparently other processes taking place which a satisfactory theory would have to allow for.

The results of these laboratory experiments show that when a hair is in saturated air, and when the humidity of this air is reduced, an increase in length of the hair occurs. Without a knowledge of this fact one would interpret the change in length as indicating a supersaturation of the air. For this reason we are of opinion that corresponding changes in hair-length in a balloon meteorograph cannot with any certainty be attributed to supersaturation. As the hygrometer in the balloon rises through a cloud it passes through a region of saturated air to air at lower relative humidity. It is likely, therefore, to show an initial expansion such as we obtained for the hair at a relative humidity of 100 per cent, when the relative humidity was decreased, for this preliminary change in length is immediate, while the change to the final length characteristic of the final relative humidity is slow.

If we compare our results with the recent experiments of Grundmann we would not expect him to have obtained the initial contraction on cooling a hair at a constant relative humidity, since he lowered his temperature much more slowly. He exhausted his chamber to a pressure of 1 mm. between the successive changes in relative humidity at a constant temperature, and this would account for his not observing the apparent supersaturation.

But the two sets of results differ in the sign of the expansion coefficient. Grundmann observes a positive coefficient over the range $+20^{\circ}$ to -50° C., whereas our coefficient changes from negative to positive as the temperature falls through $+1.5^{\circ}$ C. The main difference in the two sets of experiments appears to be in the load on a single hair, 0.5 g. in his case and 1.5 g. in ours.

§ 4. ACKNOWLEDGMENT

These experiments were carried out at the suggestion of Dr S. H. Piper, to whom we are grateful for many helpful discussions and advice.

REFERENCES

- (1) DINES. "The Dines balloon meteorograph and the method of using it." *Air Ministry M.O.* 321.
- (2) ——— "Mean values of the relative humidity at different heights in the atmosphere over England." *Quart. J. R. met. Soc.* **59**, 157.
- (3) GRIFFITHS. *Proc. phys. Soc.* **34**, 30.
- (4) PFEIFFER. *Beitr. Geophys.* **38**, 196 (1933). *Sci. Abst. A*, **36**, No. 1813, p. 450.
- (5) GRUNDMANN. *Z. InstrumKde*, **54**, 441-51 (Dec. 1934).
- (6) WALKER and ERNST. *J. industr. Engng Chem., Anal. Ed.*, **2**, No. 2 (April 1930).
- (7) WHIPPLE. "The theory of the hair hygrometer." *Proc. phys. Soc.* **34**, 1.

A bibliography up to the year 1922 is given in *Proc. phys. Soc.* **34**, xciv.

THE VISCOSITIES OF SOME LIQUID REFRIGERANTS

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ABSTRACT. The viscosities of sulphur dioxide, ethyl chloride, methyl chloride, cis-dichlorethylene, trans-dichlorethylene, trichlorethylene and dichlor-difluormethane have been measured at temperatures between -15° and $+30^{\circ}$ C. The method used is that of timing the rate of fall of a closely fitting plug in a vertical tube filled with the liquid. In order to avoid evaporation, with the resultant formation of bubbles, an auxiliary reservoir of the fluid was connected with the experimental tube; the refrigerant in the reservoir was maintained at a temperature slightly above that of the tube, so that the pressure in the apparatus was above the vapour pressure of the liquid in which the plug moved. In all cases the viscosity η was found to follow a law $\eta = Ae^{a/T}$ where T is the absolute temperature and A and a are constants.

§ 1. INTRODUCTION

IN the selection of a refrigerant, primary consideration has to be given to such physical properties as the boiling-point and specific volume; other properties, such as the viscosity and the thermal conductivity of the liquid, become of interest when the operation of the plant is being subjected to detailed analysis.

The viscosity of the refrigerant plays an important part in determining the rate of heat transfer in the evaporator and the condenser. In both these component parts, heat has to be transferred to or from a film of liquid to the metal pipe, and it is known that, in such problems of heat transfer, a determining variable is the Reynolds number Vd/ν where V is the velocity of the fluid, d the diameter of the pipe and ν the kinematic viscosity. The exact way in which the heat transfer depends on this and other variables is not yet fully elucidated and it is hoped to study this subject soon. It is clear that no progress will be possible in this direction unless data on the viscosity are available.

The compressor of a refrigerating plant has to act as a pump and to drive the fluid round the whole cycle, from compressor to condenser and thence through the throttle valve to the evaporator. In the central part of this path the refrigerant is in the form of liquid, and the resistance to flow, if the motion is stream-line, is directly proportional to the viscosity of the liquid.

§ 2. METHOD OF MEASUREMENT

The viscosities have to be measured at temperatures above the normal boiling-points of the fluids concerned, and hence the apparatus must be completely sealed so that the liquid can be maintained under pressure. It must also be of a form easy to surround with a cooling jacket, for work at low temperatures. Under these circumstances, the falling-plug method appears the most suitable.

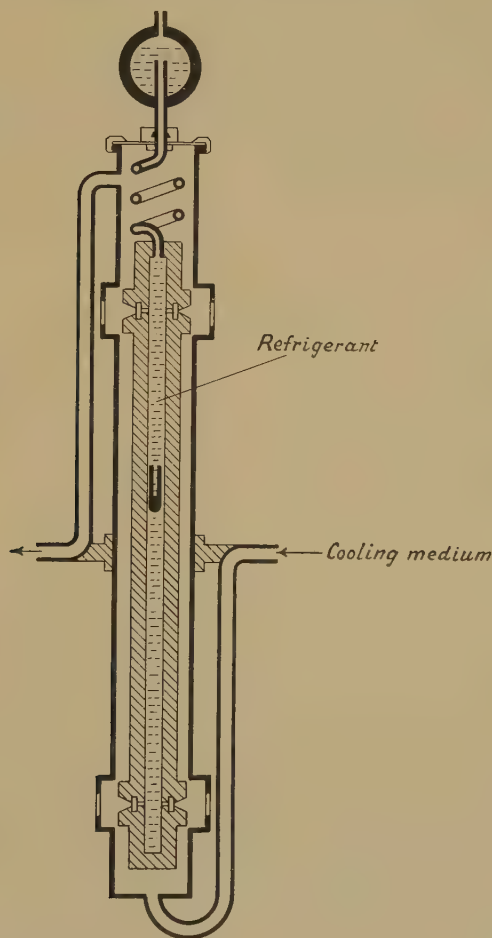


Figure 1. Viscosity apparatus (approximately quarter-scale).

The liquid was contained in a metal tube 8 mm. in diameter and 28 cm. long which had been machined so as to give it a very uniform bore. The tube was fitted with four windows in pairs diametrically opposite at each end. The windows had an aperture of about half a millimetre and a beam of light was directed through each pair. The time of transit of the plug along the central portion of the tube (22 cm.) was determined by noting the time of disappearance of the tail of the plug

at the upper windows and the appearance of the nose at the lower windows; this gave the time of passage of the plug along the uniform portion of the tube undisturbed by the presence of the holes for the windows.

In some of the experiments the windows were made of glass between lead washers. It was found that when distilled water was used as one of the liquids for calibrating the apparatus, the water attacked the lead, depositing a white film on the glass. Transparent bakelite windows held in position by invar washers were therefore used for the refrigerants other than sulphur dioxide. Liquid sulphur dioxide attacked the bakelite, so recourse was had to glass held between ebonite washers, the relative thicknesses of the glass and ebonite being so proportioned that the expansion of the unit (glass plus ebonite) was the same as that of brass. This avoided fracture of the glass window when sufficient pressure was applied between the washers to prevent leakage due to differential expansion.

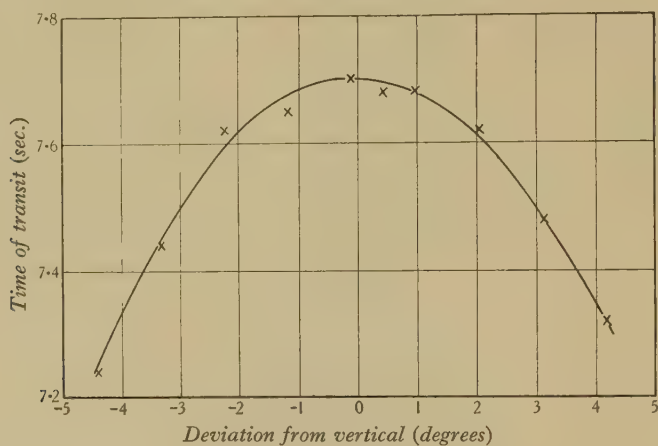


Figure 2. Effect of tilting tube.

The entire tube was sheathed in a jacket through which oil cooled by a refrigerating plant was circulated. This jacket was provided with windows in line with those in the viscosity tube.

The plug used had a cylindrical body with a hemispherical nose, and was hollowed out from the upper end so that it always fell vertically through the liquid (see figure 1). It was about 2.5 cm. long, and gave a clearance of about $\frac{1}{8}$ mm. between itself and the tube. The plug was constructed of the same brass as the tube.

Preliminary experiments with the tube filled with ether showed that the time of transit of the plug over the working section decreased appreciably when the axis of the tube deviated from the vertical. These results are shown in figure 2, where the time of transit of the plug is plotted against the deviation from the vertical in a definite plane. The actual position in which the tube was used was determined by finding the position at which the maximum time occurred, first in the plane to which figure 2 refers, and then in a plane perpendicular to this.

The apparatus was calibrated by observing the time of transit of the plug when the tube contained benzene, ether, pentane or water, each at a series of different temperatures. The viscosities of these materials were taken from the International Critical Tables, and they cover the sevenfold range from 0.24 to 1.68 centipoise. In figure 3, the results of the calibration are shown by plotting $T(\rho - \rho')$ against η , where T is the time of fall, ρ the density of the plug (8.6 g./cm.³) and ρ' that of the liquid concerned, whilst η is its viscosity. It is worthy of note that the calibration points for benzene and water agree, although their densities differ by 12 per cent. Similarly, agreement is found between ether and pentane,

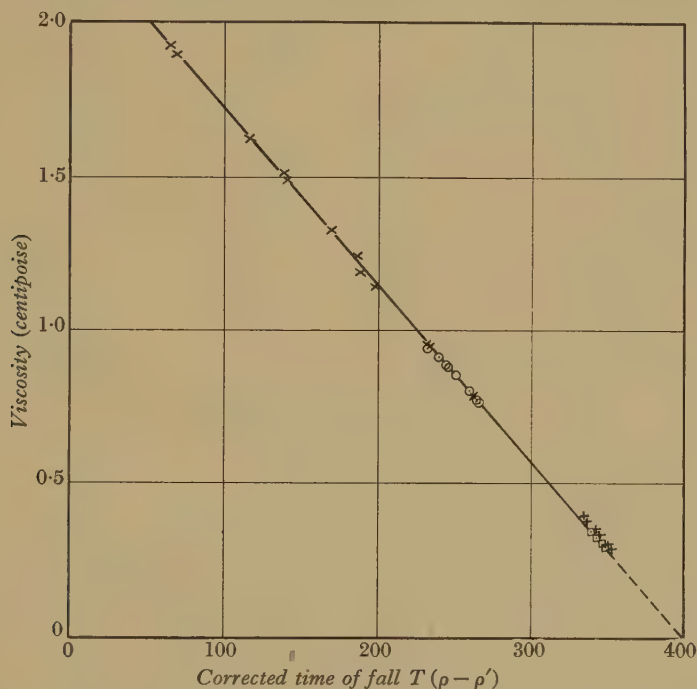


Figure 3. Calibration of apparatus. Water \times , benzene \odot , ether $+$, pentane \square .

which differ by 11 per cent in density. This may be taken as evidence that the conditions under which the plug falls are such that the time of fall between the two windows depends only on the absolute, and not on the kinematic, viscosity. After the conclusion of the series, the calibration was repeated and found to have changed slightly. In preparing table 1 giving the smoothed results, the mean of the two calibration curves has been employed.

§ 3. RESULTS

In dealing with any one substance, three observations of the time of fall were taken at each temperature, using a stop watch divided to fifths of a second. In every case at least two samples of the liquid were used, to ensure that the results obtained in the first series had not been vitiated by accidental contamination with

impurities, or by the presence of a bubble of air or vapour. In each case, the results were also examined for a possible variation of viscosity with pressure over the small range of pressures used in the experiments concerned, but in no case could such a variation be detected with certainty.

As a typical example, figure 4 shows the results for sulphur dioxide. It will be seen that the observations taken at pressures above an arbitrary limit of 3.9 atmospheres agree with those taken below.

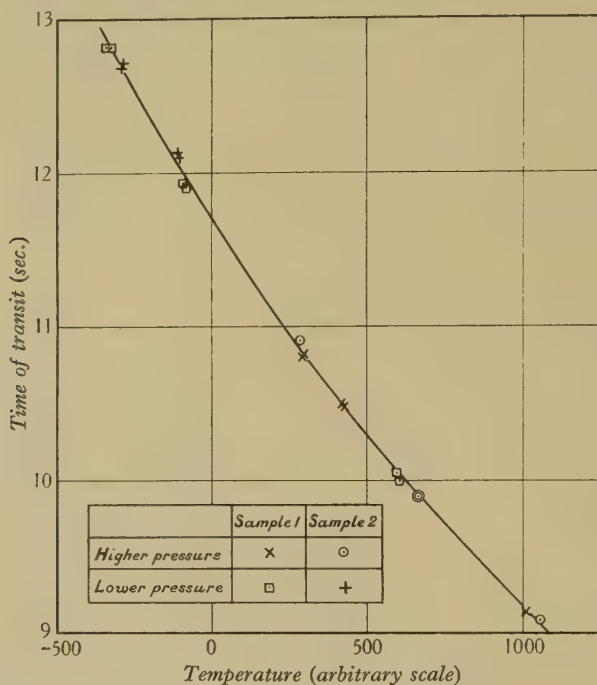


Figure 4. Sulphur dioxide.

The results for all the substances examined obey laws of the form $\eta = Ae^{a/T}$ where η is the viscosity and T the absolute temperature. Thus the experimental results lie on a straight line if the logarithm of the viscosity is plotted against the reciprocal of the absolute temperature. The observations plotted in this way for ethyl chloride, methyl chloride, cis-dichlorethylene, trans-dichlorethylene, trichlorethylene, dichlor-difluormethane (Freon) and sulphur dioxide are shown in figures 5 and 6, in which the reduction has been based on the initial calibration curve. Two samples of trans-dichlorethylene were studied, one of which contained about 10 per cent of the cis-compound, whilst the other was of higher purity. The viscosities only differed by about $\frac{1}{3}$ per cent. Values read from these curves and expressed as viscosities instead of logarithms are given in table 1, and it is of interest to notice that, despite the variety of compounds used, the viscosity of the most viscous is only about three times that of the most mobile.

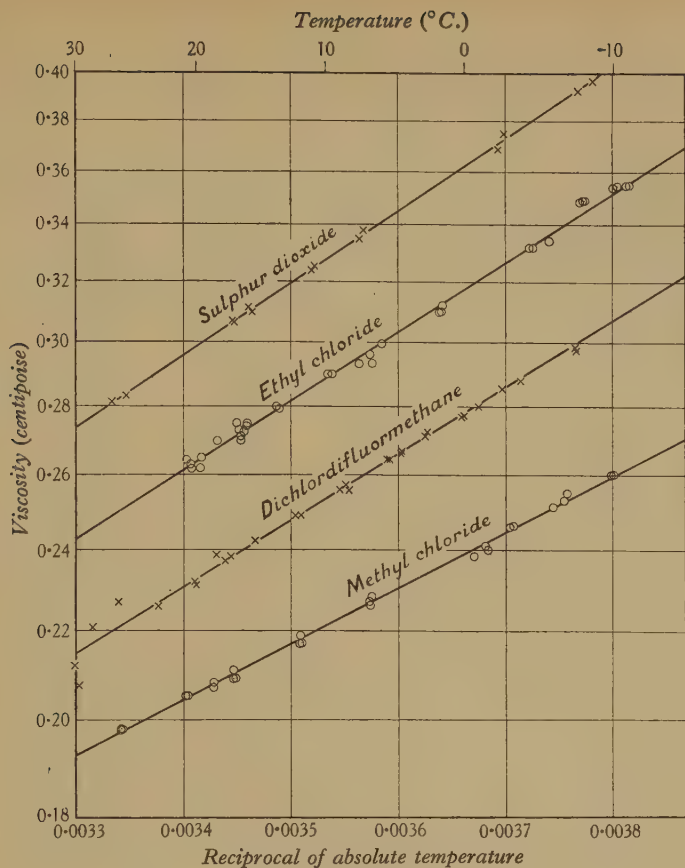


Figure 5.

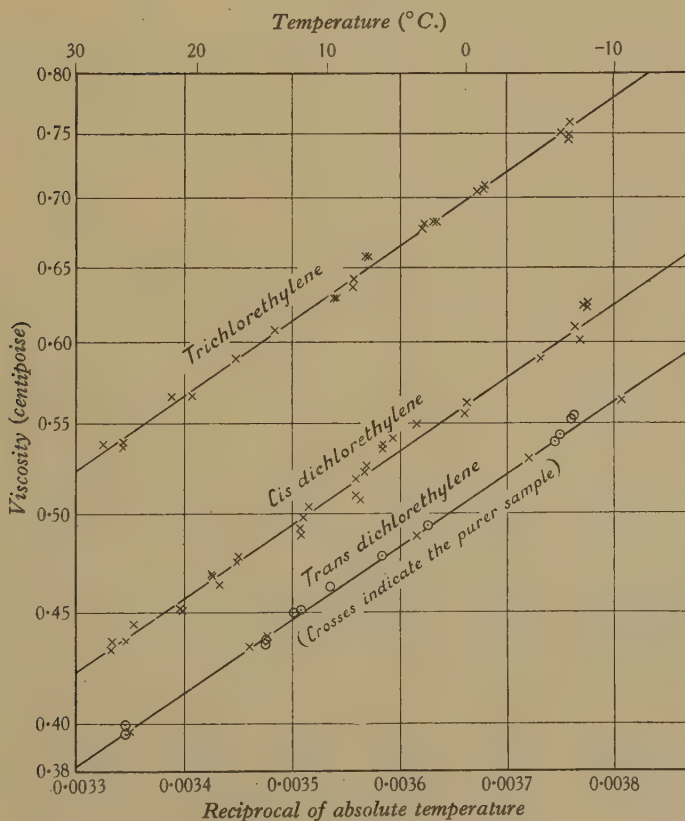


Figure 6.

Table 1. Viscosities of liquid refrigerants (centipoise)

Temperature	Methyl chloride CH ₃ Cl	Dichlorodifluoromethane CCl ₂ .F ₂	Ethyl chloride C ₂ H ₅ Cl	Sulphur dioxide SO ₂	Trans-dichloroethylene CHCl:CHCl	Cis-dichloroethylene CHCl:CHCl	Trichloroethylene CHCl ₃
30	0.19 ₇	0.21 ₉	—	0.27 ₉	0.39	0.43	0.53
25	0.20 ₃	0.22 ₇	0.25 ₉	0.29 ₁	0.41	0.45	0.56
20	0.21 ₀	0.23 ₇	0.26 ₉	0.30 ₄	0.42 ₅	0.47	0.58
15	0.21 ₇	0.24 ₇	0.28 ₀	0.31 ₈	0.44	0.49	0.61
10	0.22 ₅	0.25 ₈	0.29 ₃	0.33 ₄	0.47	0.52	0.64
5	0.23 ₄	0.27 ₀	0.30 ₈	0.35 ₀	0.49	0.54	0.67
0	0.24 ₃	0.28 ₃	0.32 ₃	0.36 ₈	0.52	0.57	0.71
-5	0.25 ₄	0.29 ₈	0.33 ₉	0.38 ₉	0.54	0.60	0.75
-10	0.26 ₅	0.31 ₃	0.35 ₈	0.41 ₀	0.57	0.64	0.79
-15	0.27 ₆	0.32 ₂	0.37 ₈	0.43 ₄	0.61	—	—

The compositions of the various materials, as obtained by chemical analysis, are also recorded below.

§ 4. CHEMICAL EXAMINATION OF SOME OF THE REFRIGERANTS*

Dichlorodifluormethane, CF₂Cl₂. This sample was tested for moisture and hydrochloric acid.

161 g. of the specimen were passed through phosphorus pentoxide tubes; the gain in weight of the latter was not measurable. 5 cm.³ of the specimen with 5 cm.³ of methyl alcohol and 4 drops of saturated solution of silver nitrate in methyl alcohol gave only a very slight turbidity.

The volume remaining undissolved after shaking 200 cm.³ of the vapour with medicinal paraffin was only 3.2 cm.³ When 100 cm.³ were distilled the whole of the liquid distilled over at a temperature of -31° C. The specimen appears to be exceptionally pure for a commercial product.

Cis-dichlorethylene, CHCl:CHCl.

Table 2. Distillation range of cis-dichlorethylene

Temperature (°C.)	48-57	57-58	58-59.4	59.4-60.4	60.4-60.7	Residue
Fractions (per cent by weight)	6	10	11	67½	4	1½

The specific gravity at 15.5/15.5° C. was 1.2919. Acidity was very slight. No free chlorine was detected.

The figures for the distillation range indicate that the liquid is nearly pure cis-dichlorethylene and the content of trans-dichlorethylene is probably much less than 5 per cent since the first fraction (48-57°) contains a small amount of water which would account for the low boiling temperatures.

* The statements as to the purity of the materials given here are summarized from reports of analyses made at the Chemical Research Laboratory, Teddington.

Trans-dichlorethylene, $\text{CHCl} : \text{CHCl}$.

Table 3. Distillation range of *trans*-dichlorethylene

Temperature (°C.)	47-48	48-48.8	48.8-50.2	50.2-51.4	51.4-53.2	53.2-59.3	Residue
Fractions (per cent by weight)	5½	6	59	12	4	9½	4

The specific gravity at 15.5/15.5° C. was 1.2664. The acidity was very slight. No free chlorine was detected.

The figures for the distillation range indicate that the liquid probably contains over 10 per cent of the *cis*-dichlorethylene. (This sample is one of the two referred to in § 3. The purer sample consisted of the fraction of the original sample which boiled in the range 48.8-50.2° C.)

Methyl chloride, CH_3Cl . The methyl chloride supplied by the Imperial Chemical Industries was stated by them to be of a purity about 99.9 per cent.

Sulphur dioxide, SO_2 . The gaseous phase contained 0.0025 per cent of weight of water and the liquid phase 0.025 per cent of water.

§ 5. DISCUSSION OF RESULTS

According to the theory of Kudar⁽¹⁾ the formula governing the variation of viscosity with temperature for an unassociated liquid should be $\eta = Ae^{Q/RT}$ where R is the gas-constant and Q the latent heat of fusion of the substance. Unfortunately these latent heats are unknown for the refrigerants tested, and therefore the truth of his theory cannot be tested. It is, however, of interest to calculate from figures 5 and 6 what the latent heats must be if the theory is true.

Table 4. Latent heats predicted by Kudar's theory

Substance	Dichlor- difluor- methane	Tri- chlor- ethylene	Trans- dichlor- ethylene	Cis-di- chlor- ethylene	Ethyl chloride	Sulphur dioxide	Methyl chloride
Latent heat of fusion (cal./g.)	11.73	11.82	16.35	16.53	22.71	23.87	24.31

A second method of estimating the latent heats of fusion is by an indirect comparison with the known latent heats of other substances. In Kaye and Laby's tables, the latent heats of eight compounds melting between -75° C. and +333° C. are given. From these data the mean value of ML/T , where M is the molecular weight, L the latent heat and T the melting point on the absolute scale is found to be 8.88 for the four with the lowest melting points (mean -14° C.) and 9.25 for the other four (mean 191° C.).

The melting point of dichlor-difluormethane is unknown, and the mean for the other six substances dealt with in the paper is -88°C . If we assume therefore that ML/T for them would have a value about 8.75, obtained by extrapolation, then the latent heats can be estimated as shown in table 5.

Table 5

Substance	Tri-chlor-ethylene	Trans-dichlor-ethylene	Cis-di-chlor-ethylene	Ethyl chloride	Sulphur dioxide	Methyl chloride
Latent heat from viscosity	11.8	16.4	16.5	22.7	23.9	24.3
Latent heat by comparison with other substances	12.4	17.4	20.1	18.2	27.4	30.4

Close agreement cannot be expected, since the values assessed by comparison with other substances are likely to be in error by quite large amounts. Nevertheless, the order of magnitude is the same by the two methods, and thus the viscosity data appear to support the theory of Kudar, at least approximately. It is hoped to measure the latent heats of fusion of these materials in the near future, and thus to check the theory more accurately.

§ 6. ACKNOWLEDGMENTS

The work recorded in this paper was carried out at the request of the Engineering Committee of the Food Investigation Board, to whom we are indebted for permission to publish.

We are deeply indebted to Dr Guy Barr for his extremely helpful advice at various stages of the work, and we wish also to thank Mr A. Snow for his skilful assistance both in the constructional and the observational work.

REFERENCE

- (1) KUDAR, H. C. *Z. Phys.* **80**, 217 (1933).

536.212.2.022:537.723.1:669.018.45

THE THERMAL AND ELECTRICAL CONDUCTIVITIES OF METALS AND ALLOYS: PART 2, SOME HEAT-RESISTANT ALLOYS FROM 0° C. TO 800° C.

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ABSTRACT. A comparative longitudinal-flow method has been used to determine the thermal conductivities, up to temperatures approaching 800° C., of F.N.C.T., F.H. stainless, Staybrite and Era A.T.V. steels, and of monel metal and an alloy composed of approximately 80 per cent of nickel and 20 per cent of chromium. The values are derived in terms of the thermal conductivity of a specimen of nickel-plated iron which had been previously tested over the full temperature-range. Determinations of the electrical resistivity are made in the course of the same experiment, and values of the Lorenz function are derived. Whereas at atmospheric temperature the values of the Lorenz function for these metals are abnormally high, and vary from 0.76×10^{-8} for the F.N.C.T. steel to 1.18×10^{-8} for the F.H. stainless steel, they decrease towards a common value with increase in temperature, and at 800° C. all lie between 0.62×10^{-8} and 0.68×10^{-8} . An examination of values obtained for the Lorenz function of metals by other workers reveals that the extreme values so far published for this function over the temperature-range 400° to 1000° C. are 0.56×10^{-8} and 0.80×10^{-8} . It is concluded that the thermal conductivity of a metal can be predicted with a fair degree of approximation over this range of temperature from a knowledge of the electrical resistivity, and that in general the probable error involved decreases as the temperature increases.

§ 1. INTRODUCTION

THIS paper forms part of a research which is directed towards an investigation, over a wide range of temperature, of the extent to which pure metals and various alloys obey the Wiedemann-Franz-Lorenz law.

At the time at which the work was commenced there was a scarcity of thermal-conductivity data for the stainless steels and nickel-chromium alloys, particularly at the high temperatures at which these heat-resistant alloys are frequently used in practice. Determinations made at moderate temperatures had indicated that in general these metals possessed a low thermal conductivity, and that the value of the Lorenz function might be expected to be abnormally high. It appeared, therefore, that measurements of the thermal and electrical conductivities of several commercial alloys of this type up to temperatures of the order of 800° C. might furnish results of considerable academic interest which should also be of practical value. During last year M. S. van Dusen and S. M. Shelton^(1, 2) working at the Bureau of Standards have published values of the thermal conductivity of a number of

alloys of this class over a temperature-range of 100–550° C. The method which they employed was similar in principle to that which had been used for the present investigation, and it is satisfactory that in those cases in which materials of similar compositions have been tested the values are in good agreement.

§ 2. DESCRIPTION OF METALS TESTED

In each instance the specimens were obtained in the form of rods, approximately 3 in. in diameter and 15 in. long. Table 1 contains a description and analysis of the metals tested.

§ 3. METHOD OF EXPERIMENT

(i) *Range 30–200° C.* The rods were each machined to a uniform diameter of a little less than 3 in., and one end was fashioned so as to fit into the machined end of one of the Armco iron rods previously tested⁽³⁾. Holes for the insertion of thermocouples were drilled normal to the surface at distances of 6.0 and 25.4 cm. from this machined end. To this end was soldered a water-flow calorimeter, and the rod was then mounted vertically with the calorimeter uppermost, within a lagged guard tube about 6 in. in diameter. To prevent convection currents being set up the interspace was packed with silocel insulating powder. The rod was electrically heated at the base, and the guard tube adjusted to prevent lateral interchange of heat. The quantity of heat flowing in the rod was determined in terms of the rise in temperature of the water which flowed at a steady measured rate through the calorimeter. This temperature-rise was measured by means of differential thermocouples, and in order that it should remain constant in value the water was passed through a coil immersed in a thermostatically controlled bath immediately before entering the calorimeter. The latter and the tubes containing the thermocouple junction were well lagged to prevent any appreciable heat-interchange taking place. The temperature-gradient established in the specimen was measured by means of a single thermocouple which could be inserted into either of the two holes mentioned above.

This method was not used for mean temperatures above about 200° C. as this would necessitate the determination being made with very large temperature-gradients, but it was useful as a check on the results of the main experiment; moreover it enabled values of the thermal conductivity to be determined at temperatures as low as 30° C.

Each of the specimens was first tested in this manner over the range 30–200° C., and the results obtained were in good agreement with those of the main research.

(ii) *Range 200–800° C.* The method used for the measurement of thermal conductivity at higher temperatures is essentially a comparative one, in which the water-flow calorimeter is replaced by a rod of known conductivity, and the thermal conductivity of the alloy is deduced from measurements of the temperature-gradients established in the two rods when the same quantity of heat flows in each. One of the nickel-plated rods of Armco iron already tested was used as the metal of known conductivity.

Table 1. Particulars of metals investigated

Material	Supplied by	Description	Analysis												
			Fe	C	Ni	Cr	Mn	Si	Cu	W	S	P	Mg	Al	Co
F.N.C.T. steel		Oil hardened and tempered 830°/600° C.	94.36†	0.39	3.55	0.85	0.64	0.21	—	—	?	?	—	—	—
F.H. stainless steel	Brown Firth Research Laboratories	Air hardened 940° C. Tempered 725° C.	85.15†	0.27	0.37	13.65	0.29	0.27	—	—	?	?	—	—	—
Staybrite steel		Softened 1150°/1200° C.	73.49†	0.15	8.04	17.87	0.26	0.19	—	—	?	?	—	—	—
*Era A.T.V. steel	Hadfields, Ltd.	Forged steel	52.2†	0.46	26.86	15.20	1.18	1.30	—	2.77	0.014	0.018	—	—	—
*Monel metal	Monel-Weir, Ltd.	Hot rolled, black surface	1.72	0.16	67.10	—	0.98	0.01	29.18	—	0.014	0.024	0.13	0.04	0.33
*Coronil (70 Ni, 30 Cu)	H. Wiggin and Co., Ltd.	Forged and drawn	0.60	0.10	68.41	—	1.17	0.4	28.94	—	—	—	0.16	—	—
Nichrome (80 Ni, 20 Cr)	H. Wiggin and Co., Ltd.	Forged and drawn	0.59	0.12	77.28†	20.98	0.65	0.38	—	—	—	—	—	—	—

* The author is indebted to Mr T. E. Rooney of the Metallurgy Department, National Physical Laboratory, for these analyses, and to the manufacturers for the other analyses and descriptions.

† These figures have been derived by difference.

In order to join the test specimen to the iron a tin bath was first used. This proved satisfactory during assembly and at the lower temperatures, but after pro-

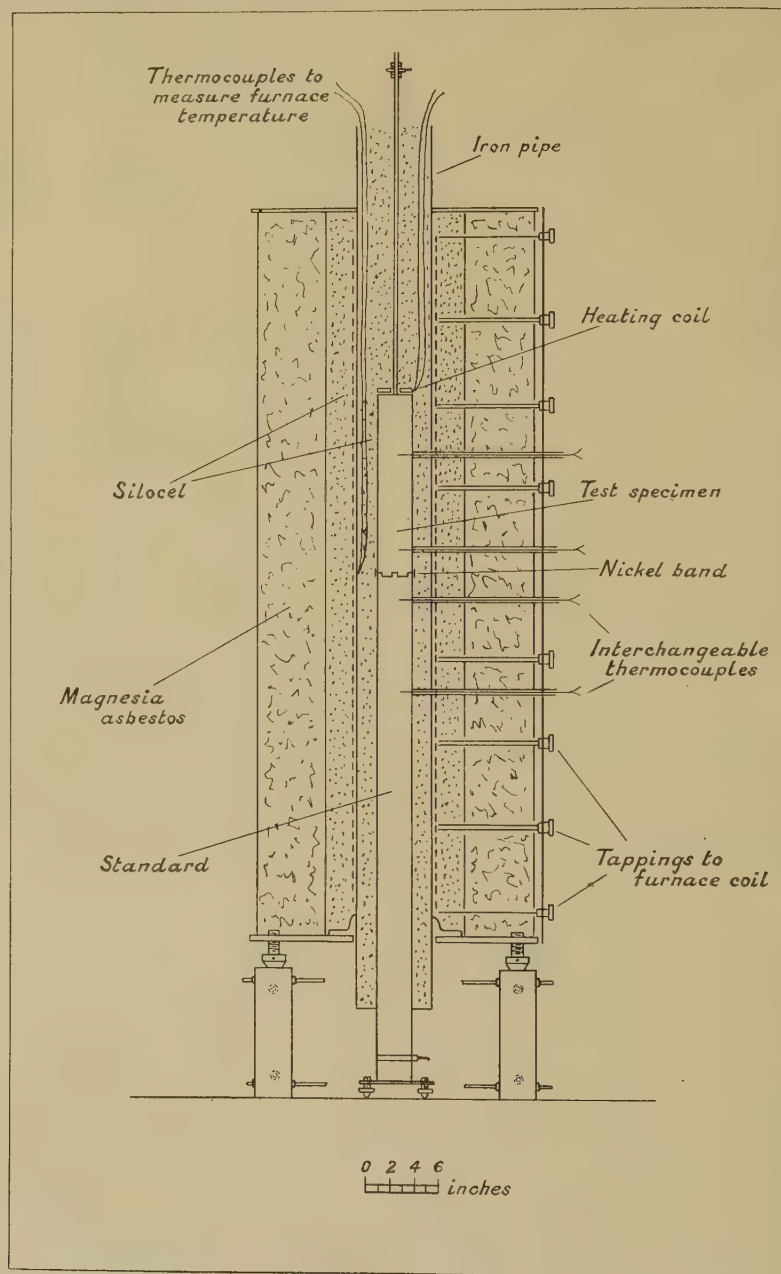


Figure 1. Apparatus for measuring thermal conductivity.

longed heating at high temperatures the tin underwent oxidation, and the thermal contact between the rods became unsatisfactory. It was afterwards found that good

thermal contact could be maintained if, in addition to the tin bath, a strip of nickel about 0.2 cm. thick and 1.5 cm. wide was screwed into position so as to form a band covering the junction of the rods. When the rods were being joined together care was taken to ensure that they should be in line with one another, and that all four thermocouple holes should be in one plane. Three thermocouples composed of fine platinum and platinum-rhodium wires were pegged into small holes drilled in each rod, and a steel rod $\frac{1}{2}$ in. in diameter and 2 ft. in length was screwed into the centre of the upper end of the test bar.

The composite rod, with the test specimen uppermost, was then lowered into position in the furnace which had been used for the earlier measurements on the

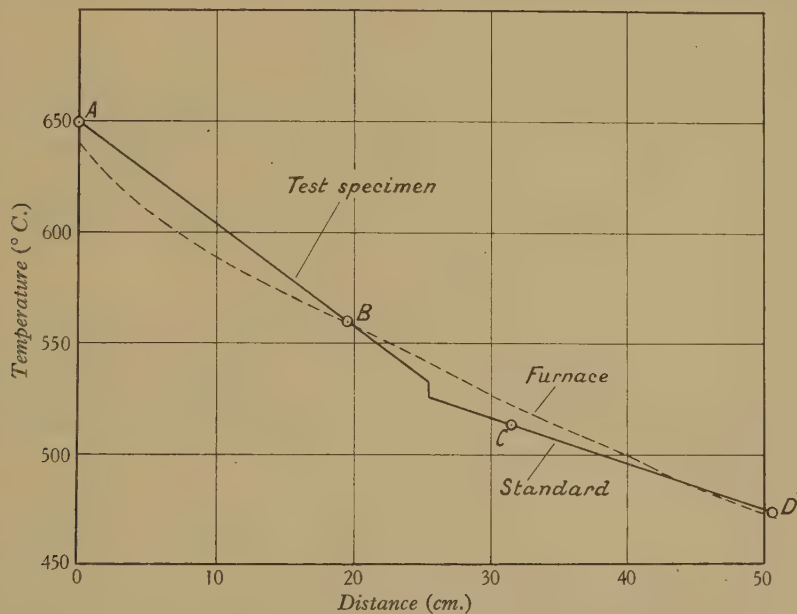


Figure 2. Example of temperature-distributions of central rods and furnace.

iron rods. The thermocouple holes were aligned with those in the furnace wall and the silica sheaths were inserted. A nichrome heating-coil wound in a flat spiral and embedded in a disc of steatite was dropped over the projecting steel rod on to the upper end of the specimen, and the furnace was packed with silocel powder. The steel rod served as one electrode when the resistance of the alloy was being measured, the other electrode being pegged into the lower end of the iron rod. The assembled apparatus is shown in figure 1.

The actual experimental method was very similar to that already described in the case of iron, except that in this instance no measurements were made of the electrical energy supplied to the specimen. Instead, this was derived in terms of the thermal conductivity of the standardized rod, and the measured temperature gradient therein, when lateral interchange of heat was prevented by carefully matching corresponding points of the rod and surrounding tube. Owing to the

sudden change in gradient which occurred at the junction of the two metals an exact match was not always possible, and in these cases a small correction has to be applied before the true thermal conductivity of the alloy can be obtained. A typical example of the temperature-distributions of the furnace and centre rods is shown in figure 2, and this may be used to illustrate the manner in which the correction is derived. The points marked *A*, *B*, *C* and *D* denote the positions and temperatures of the rod recorded by the interchangeable thermocouple; *C* and *D* are in the standard, and *A* and *B* in the test material, Era A.T.V. It will be observed that there is a drop of about 7° C. at the junction of the two rods, but the effect of this does not appear to be serious provided that the adjacent furnace is not too different in temperature. The mean temperature of the furnace is given by the dotted line.

x, a, b, c

Let x represent the heat flowing in the specimen at *A*, and a , b and c (with the appropriate signs) the heat gained or lost laterally over the sections *AB*, *BC* and *CD* respectively. The gradient dT_T/dl_T in the test specimen of area A_T and conductivity K_T can be assumed to be established by the mean energy flowing in the section *AB*,

i.e.

$$K_T A_T dT_T/dl_T = x + a/2,$$

and similarly for the standard (suffix *S*)

$K_S, A_S,$

$$K_S A_S dT_S/dl_S = x + a + b + c/2,$$

T_S, l_S

giving $K_T A_T dT_T/dl_T = K_S A_S dT_S/dl_S - a/2 - b - c/2$. Approximate values for a , b and c can be obtained by means of the equation for radial heat-flow h which, however, is only strictly true in the absence of a longitudinal gradient. Thus

h

$$h = \frac{2 \cdot 73 K (T_S - T_F) L}{\log_{10} r_F/r_S},$$

K, T_F

where K is the thermal conductivity of the lagging-material, $(T_S - T_F)$ the mean difference in temperature between the specimen and furnace over the section of length L , and r_S and r_F are the respective radii of the specimen and the furnace. Assuming the thermal conductivity of silocel to be 0.0002 c.g.s. unit the values of a' , b' and c' become respectively 0.035, 0.022 and 0.035 calories per degree of mean difference in temperature between the specimen and furnace. The actual mean differences in temperature for the three sections are 10.7°, 8.1° and 2.7° C. From which it is seen that $a = -0.378$, $b = 0.178$, and $c = 0.095$ calories.

L, r_S, r_F

For this particular experiment the temperatures at *A*, *B*, *C* and *D* are 648.2, 559.8, 512.9 and 473.1 respectively; $L_T = L_S = 19.4$ cm., $A_T = 42.32$ cm², $A_S = 42.45$ cm², and at 493° C. $K_S = 0.1056$ c.g.s. unit. Hence $K_T = 0.0479$ c.g.s. unit. This is the thermal conductivity of the test specimen at a mean temperature of 604° C. In this experiment the correction for the lateral heat-transfer amounted to 0.4 per cent of the heat flowing in the standard rod.

At each mean temperature the relative temperatures of the furnace and specimen were adjusted so that the above correction assumed both positive and negative values, and the mean conductivity was determined from about six experiments of this kind.

The electrical conductivity was measured at the same time by passing a current of the order of 60 amperes through the rod, and comparing the potential-drop down a section of the rod with that across a standardized resistance connected in series with it. The thermocouples attached to the rod were used as the potential leads, the direction of the current being reversed in order to enable thermal e.m.f.s. to be eliminated. In this manner determinations of the thermal and electrical conductivity of each alloy were made at a series of increasing mean steady temperatures up to nearly 800° C. A few repeat points were obtained during cooling, and in no instance did the difference due to heat treatment exceed 4 per cent.

§ 4. TABULATED RESULTS AND COMPARISON WITH OTHER WORKERS

In the tables which follow the values of the thermal conductivity K , in c.g.s. units, the electrical resistivity ρ in ohm-cm. and the Lorenz function, $K\rho/T$, where T is the absolute temperature, have been interpolated from the experimental results for every 100° C. from 0° to 800° C. A certain amount of extrapolation has been necessary in deriving the values at the two extreme temperatures of 0° and 800° C., and the values are bracketed for this reason. Reference is made to the results obtained by other workers where these are available for materials of similar compositions.

K
 ρ

(a) *F.N.C.T. steel*

Temp. (° C.)	0	100	200	300	400	500	600	700	800
Property									
K	(0.080)	0.086	0.089	0.090	0.088	0.084	0.075	0.067	(0.059)
$10^6 \times \rho$	(26.0)	31.7	38.4	46.3	55.7	67.0	80.3	98.4	(124)
$10^8 \times K\rho/T$	(0.76)	0.73	0.72	0.72	0.73	0.72 ₅	0.69	0.67 ₅	(0.68)

(b) *F.H. stainless steel*

Temp. (° C.)	0	100	200	300	400	500	600	700	800
Property									
K	(0.058 ₅)	0.060	0.061	0.061 ₂	0.061 ₃	0.061 ₄	0.061 ₃	0.059	(0.056 ₅)
$10^6 \times \rho$	(55.0)	63.4	71.8	80.2	88.5	97.0	105.6	114.1	(122.7)
$10^8 \times K\rho/T$	(1.17 ₇)	1.02	0.92 ₈	0.85 ₇	0.80 ₆	0.77 ₂	0.74 ₁	0.69 ₂	(0.64 ₈)

S. M. Shelton⁽²⁾ measured the thermal conductivity of two chromium steels somewhat similar to the above, the analyses and values being:

Chemical composition							Thermal conductivity at various temperatures (° C.)				
C	Mn	P	S	Si	Ni	Cr	100	200	300	400	500
0.07	0.09	0.015	0.010	0.09	0.23	12.00	0.0595	0.0619	0.064	0.0662	—
0.14	0.19	0.020	0.015	0.12	0.70	14.60	0.0581	0.0590	0.0602	0.0612	0.0625

These values are seen to be in reasonably good agreement with those obtained in the present investigation.

(c) Staybrite steel

Temp. (° C.) Pro- perty	0	100	200	300	400	500	600	700	800
K	(0.035 ₅)	0.039	0.042	0.045	0.049	0.052	0.056	0.059	(0.062 ₅)
$10^6 \times \rho$	(66.3)	74.3	81.9	89.1	95.0	100.1	104.8	109.4	(114.0)
$10^8 \times K\rho/T$	(0.86 ₅)	0.77 ₄	0.72 ₇	0.70 ₄	0.69	0.67 ₃	0.67	0.66 ₄	(0.66 ₄)

S. M. Shelton⁽²⁾ has also examined three "18/8" stainless steels having similar compositions to this alloy, and obtained values in agreement with the present determination. Data for his specimens are set out below.

Chemical composition				Thermal conductivity at various temperatures (° C.)				
C	Mn	Ni	Cr	100	200	300	400	500
0.07	0.27	9.10	18.6	0.0392	0.0423	0.0454	0.0485	0.0516
0.11	0.19	9.21	18.5	0.0390	0.0421	0.0452	0.0480	0.0511
0.24	0.37	8.96	19.6	0.0373	0.0411	0.0447	0.0483	0.0519

The value of 0.033 is given for the thermal conductivity of Staybrite steel in *The development of Staybrite steel—Its properties and uses*, published by Thos. Firth and Sons, Ltd. The specific resistance in the fully softened condition is stated to be 69×10^{-6} . These values are presumably at atmospheric temperature. The increase in resistance with rise in temperature of Staybrite in the heat treated condition is shown over the range 18–300° C. by means of a curve, with which the present results are in general agreement.

(d) Era A.T.V.

Temp. (° C.) Pro- perty	0	100	200	300	400	500	600	700	800
K	(0.026)	0.030	0.033	0.037	0.040	0.044	0.047	0.051	(0.054)
$10^6 \times \rho$	(98.0)	102.7	106.9	111.0	114.2	117.3	120.1	122.2	(123.6)
$10^8 K\rho/T$	(0.95)	0.82	0.75	0.71	0.68	0.66 ₅	0.65	0.63 ₅	(0.62)

(e) 80 per cent nickel and 20 per cent chromium

Temp. (° C.) Pro- perty	0	100	200	300	400	500	600	700	800
K	(0.030)	0.033 ₅	0.037 ₅	0.041 ₅	0.045	0.051	0.055	0.059	(0.063)
$10^6 \times \rho$	(107.3)	108.3	109.0	110.0	110.8	111.3	111.4	110.3	(110.2)
$10^8 \times K\rho/T$	1.14	0.98	0.86 ₅	0.79 ₅	0.74 ₅	0.73	0.70	0.67	(0.64 ₅)

Ellis, Morgan and Sager⁽⁴⁾ obtained values of 0.0358, 109.7×10^{-6} and 1.29×10^{-8} for the thermal conductivity, specific resistance and Lorenz function of an 80 per cent nickel and 20 per cent chromium alloy at a temperature of 32° C., whilst the

corresponding values obtained by Kikuchi⁽⁵⁾ at 36° C. are 0.031₂, 105 × 10⁻⁶ and 1.06 × 10⁻⁸. The present values are in general agreement with the average results from these two determinations, and with the values of the thermal conductivity obtained by van Dusen and Shelton⁽¹⁾ which are 0.325 at 100° C., 0.0368 at 200° C., 0.0411 at 300° C., 0.0452 at 400° C., and 0.0492 at 500° C. Mention might be made of the fact that the experimental results of this alloy show a discontinuity in the thermal-conductivity-temperature curve at a little below 500° C. The specific

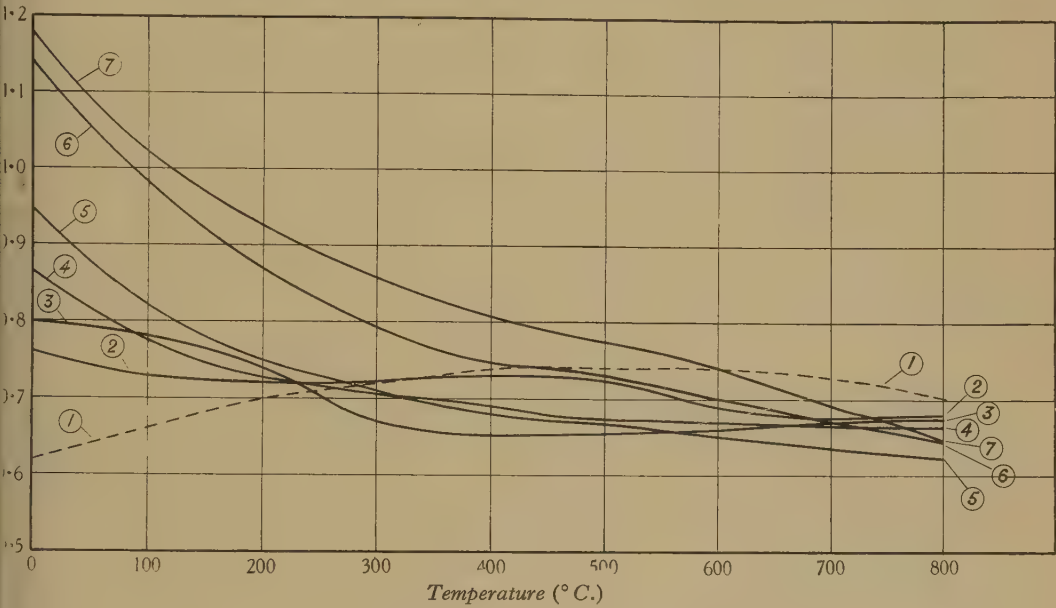


Figure 3. Variation of Lorenz function with temperature. (1) Armco iron; (2) F.N.C.T. steel; (3) Monel metal; (4) Staybrite steel; (5) Era A.T.V. steel; (6) Nichrome (80% Ni, 20% Cr); (7) F.H. stainless steel.

resistance has a maximum value at about 600° C. and the values obtained during both heating and cooling are in agreement beyond this temperature. As the metal was cooled below 530° C. the values of the resistivity increased about 2 per cent above those obtained at the corresponding temperature during heating and remained at about this level during the subsequent cooling to room temperature. It would appear that this alloy undergoes some definite change in the neighbourhood of 500° C.

(f) Monel metal

Temp. (° C.)	0	100	200	300	400	500	600	700	800
Property									
K	(0.051)	0.058	0.066	0.073	0.080	0.088	0.095	0.102 ₅	(0.110)
10 ⁶ × ρ	(42.9)	50.1	53.2	52.5	54.6	57.7	60.8	63.3	(65.7)
10 ⁸ × Kρ/T	(0.80)	0.78	0.74	0.67	0.65	0.65 ₅	0.66	0.67	(0.67 ₅)

These values for the thermal conductivity are in reasonable agreement with those published by the Mond Nickel Company Ltd.⁽⁶⁾ for metals of composition 70 per cent nickel and 30 per cent copper in the annealed condition. It is stated that a method similar to that used by Schofield⁽⁷⁾ was employed, the following values being obtained, 0.062, 0.065, 0.076 and 0.078 c.g.s. unit at temperatures 94, 288, 421 and 439° C. respectively. The value of the specific resistance at atmospheric temperature is given as 42×10^{-6} ohm-cm.

Somewhat higher values have been obtained for the thermal conductivity of alloys of approximately this composition by other workers. Donaldson⁽⁸⁾ tested a specimen of the following percentage composition, nickel 67.05, copper 29.07, iron 2.68, manganese 0.84 and silicon 0.30 and obtained values of 0.07, 0.077, 0.080 and 0.084 c.g.s. unit at 100, 200, 300 and 400° C. respectively. Smith⁽⁹⁾ records a value of 0.069 c.g.s. unit at 57° C. for an alloy of 70 per cent nickel and 30 per cent copper, whilst Ellis, Morgan and Sager⁽⁴⁾ included in the investigation, to which mention has already been made, an alloy containing 70 per cent nickel, 28 per cent copper and 2 per cent iron, and obtained values of 0.0832 c.g.s. unit, 42.6×10^{-6} ohm-cm. and 1.16×10^{-8} at a temperature of 32° C. for the thermal conductivity, specific resistance and Lorenz function respectively.

(g) 70 per cent nickel and 30 per cent copper

Tests on the alloy described in table 1 as having this approximate composition were only carried out in the lower-temperature apparatus, the results obtained being similar to those given by monel metal. The values of the thermal conductivity could be represented by a straight line extending from 0.051 c.g.s. unit at 0° C. to 0.069 at 200° C. The electrical resistivity at atmospheric temperature was 46×10^{-6} ohm-cm.

§ 5. DISCUSSION OF THE RESULTS FOR THE LORENZ FUNCTION

The results obtained for the Lorenz function of the alloys tested are plotted in figure 3. It will be seen that in the neighbourhood of atmospheric temperature there are considerable departures from the normally accepted value of about 0.55×10^{-8} . The present values invariably exceed this figure, those for the nickel-chromium alloy and F.H. stainless steel being more than twice as great. Had the Wiedemann-Franz-Lorenz law been assumed to hold good for these alloys, and an attempt made to derive the value of the thermal conductivity from a knowledge of the electrical resistance, the value obtained would have been less than half of the true value.

With increase in temperature the values of the Lorenz function are seen to alter considerably and to tend towards mean values of about 0.7×10^{-8} at 600° C. and 0.65×10^{-8} at 800° C. From this result it is apparent that the thermal conductivity of alloys of the type considered can be deduced indirectly from electrical-resistance measurements with considerably greater certainty at higher temperatures. By assuming the aforementioned mean values for the Lorenz function the thermal

conductivity could presumably be predicted to within 10 per cent over the temperature-range 600–800° C. At present there is a scarcity of experimental data for metallic conductors at high temperatures and this conclusion may prove to be somewhat limited in its range of applications. A certain amount of support for a convergence of values of the Lorenz function as the temperature is increased is, however, given by the results of Lees⁽¹⁰⁾ and other workers at low temperatures. The values of the Lorenz function for the metals bismuth and antimony, and the alloys German silver, manganin, platinoid and lipowitz metal are all abnormally high at a temperature of –170° C., ranging from 1.56×10^{-8} to 0.90×10^{-8} for the last-mentioned four, but decrease as the temperature is increased, so that at 18° C. the values lie within the limits 0.81×10^{-8} and 0.72×10^{-8} . On the other hand highly conducting metals, such as copper and aluminium, possess abnormally low values of the Lorenz function at extremely low temperatures, which increase to values mostly lying between 0.5×10^{-8} and 0.6×10^{-8} at atmospheric temperature, and frequently continue to increase slowly with further increase in temperature.

With regard to determinations at high temperatures, Schofield⁽⁷⁾ has shown that the value for copper increases only from 0.55×10^{-8} to 0.57×10^{-8} , and then decreases slightly again over the range from 100° to 600° C., whereas for aluminium it increases from 0.53×10^{-8} at 100° C. to 0.60×10^{-8} at 400° C. For nickel the value increases up to the temperature of the magnetic transformation point and thereafter remains fairly constant to 700° C., having a value of about 0.64×10^{-8} .

Holm and Störmer⁽¹¹⁾ have measured the thermal and electrical conductivities of platinum over the range 19–1020° C., and have found the Lorenz function to increase from 0.61×10^{-8} to a maximum of $0.71_5 \times 10^{-8}$ at about 800° C. and then decrease to $0.68_5 \times 10^{-8}$ at 1020° C.

Honda and Simidu⁽¹²⁾ tested nickel, Swedish iron, and a number of carbon steels up to about 900° C., and an examination of their data shows that over the temperature-interval 600–900° C. all values for the Lorenz function lie between 0.64×10^{-8} and 0.80×10^{-8} .

The only other experiments within this temperature-range which have come to the notice of the present author are those of Angell⁽¹³⁾ and Sager⁽¹⁴⁾. The former shows the Lorenz function of aluminium to increase from 0.54×10^{-8} to 1.21×10^{-8} over the range 100–600° C. and that of nickel to decrease from 0.74×10^{-8} at 300° C. to 0.34×10^{-8} at 700° C., whilst the latter gives a value as high as 1.10×10^{-8} for nickel at 700° C. Angell used the radial-flow method, and probably endeavoured to deal with too small a difference in temperature, whilst Sager, who also tested a number of nickel-copper alloys, adopted King's⁽¹⁵⁾ suggested periodic-flow method for measurements at high temperature. The term used in the equation to represent the heat-loss from the surface due to radiation is a function of the difference in temperature between the wire under test and the enclosure, instead of the difference between the fourth powers of these temperatures, which may account for the high values obtained for the thermal conductivity at high temperatures.

When the results of these last two experiments are omitted it is found that the values of the Lorenz function of all metals so far tested over the range 400–1000° C. lie between 0.56×10^{-8} and 0.80×10^{-8} .

§ 6. ACKNOWLEDGMENTS

In conclusion the author desires to thank the Superintendent of the Physics Department for providing the facilities necessary to conduct this research, and to acknowledge his indebtedness to Mr E. E. Smith, B.Sc., for assistance with much of the observational work. It is further desired to record thanks to Messrs Monel-Weir, Ltd. and to the Brown Firth Research Laboratories who supplied specimens free of charge for use in this investigation.

REFERENCES

- (1) VAN DUSEN, M. S. and SHELTON, S. M. *Bur. Stand. J. Res.* **12**, 429–40 (1934).
- (2) SHELTON, S. M. *Bur. Stand. J. Res.* **12**, 441–50 (1934).
- (3) POWELL, R. W. *Proc. phys. Soc.* **46**, 659–74 (1934).
- (4) ELLIS, W. G., MORGAN, F. L. and SAGER, G. F. *Engng Sci. Ser. Rensselaer*, No. 21 (Sept. 1928).
- (5) KIKUCHI, R. *Sci. Rep. Tōhoku Univ.* **12**, 585–93 (1932).
- (6) *Nickel-copper alloys containing more than 50 per cent nickel*. Publication R. 2. The Mond Nickel Co., Ltd.
- (7) SCHOFIELD, F. H. *Proc. roy. Soc. A*, **107**, 205–27 (1925).
- (8) DONALDSON, J. W. *J. Inst. Met.* **34**, 43–55 (1925).
- (9) SMITH, A. W. *Ohio Engng Exp. Sta. Bull.* **31** (1925).
- (10) LEES, C. H. *Philos. Trans.* **208**, 381–443 (1908).
- (11) HOLM, R. and STÖRMER, R. *Wiss. Veröff. Siemens-Konz.* **9**, 312–22 (1930).
- (12) HONDA, K. and SIMIDU, T. *Sci. Rep. Tōhoku Univ.* **6**, 219–33 (1917).
- (13) ANGELL, M. F. *Phys. Rev.* **33**, 421–32 (1911).
- (14) SAGER, G. F. *Engng Sci. Ser. Rensselaer*, No. 27 (June 1930).
- (15) KING, R. W. *Phys. Rev.* **6**, 437–45 (1915).

THE MECHANICAL FORCE ON BODIES OF SMALL SUSCEPTIBILITY DUE TO INDUCED MAGNETIZATION

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ABSTRACT. The mechanical force on a body of any shape and of small susceptibility, when placed in a magnetic field, is expressed as an integral taken over the surface of the body. This principle is applied to the experimental arrangement adopted in Rankine's magnetic torsion balance, where a magnetic pole is attracted by the magnetization induced in a spherical body. The results obtained are (1) a direct proof of Rankine's formula for a point pole; (2) the correction for the earth's field; and (3) the correction for the finite spread of the poles in an actual magnet.

§ 1. INTRODUCTION

RANKINE'S recent adaptation⁽¹⁾ of the magnetic torsion balance to the measurement of the paramagnetism of substances of small susceptibility has drawn attention anew to the classical problem of the calculation of the mechanical forces on a body due to its induced magnetization. In the general case we have to consider a body of specified form with uniform susceptibility κ , and an applied field of variable magnetic intensity \mathbf{H} . When no restriction is placed on the value of κ , the problem is effectively soluble only for bodies with certain specified forms, e.g. a cylinder, a sphere or an infinite plane. The only obvious general result is that the resultant mechanical force and couple due to the action of the applied field on the induced magnetization will always be zero if the applied field is uniform in magnitude and direction. In other words, the resultant force and couple are due to the non-uniformity of the applied field in the neighbourhood of the body.

In the special cases considered by Rankine, however, the susceptibility is always small, typical values being 3.2×10^{-8} for air and -7×10^{-7} for water. In these circumstances a simple and general solution, valid to a high degree of approximation, can be found in the form of an integral taken over the surface of the magnetizable body. Rankine himself has considered the particular problem of the attraction of a paramagnetic sphere by a magnetic pole and has deduced a simple, approximate expression for the force, valid for small κ , from the complex, exact expression given by Jeans for any value of κ . It is a matter of interest to obtain this particular approximate result directly and it may be easily found from the general approximate result in the form of a surface integral.

κ
 \mathbf{H}

§ 2. THE INDUCED MAGNETIZATION

The general approximate result is that the induced magnetization is equivalent to a layer of magnetic matter distributed over the surface of the magnetizable body with surface density σ equal to $\kappa H_0^{(n)}$ when $H_0^{(n)}$ is the component of the magnetic intensity of the applied field along the outward-drawn normal to the surface of the body. The error involved in this approximate result is of the order of magnitude of κ^2 , and is therefore usually negligible. This result can be established either (a) by the use of the conditions of continuity at the boundary of the magnetic media or (b) by the use of Poisson's transformation.

(a) Let the magnetic potential of the applied field \mathbf{H}_0 be V_0 and let V, U be the potentials due to the induced magnetization at points which are respectively outside and inside the magnetizable body. Then the boundary conditions at the surface S of the body are

$$V_0 + V = V_0 + U,$$

$$\frac{\partial V_0}{\partial n} + \frac{\partial V}{\partial n} = (1 + 4\pi\kappa) \left\{ \frac{\partial V_0}{\partial n} + \frac{\partial U}{\partial n} \right\},$$

where the differentiations are along n , the outward-drawn normal to S . Now V and U are expressible in the forms,

$$V = \kappa V_1 + \kappa^2 V_2 + \dots + \kappa^n V_n + \dots,$$

$$U = \kappa U_1 + \kappa^2 U_2 + \dots + \kappa^n U_n + \dots,$$

where V_n, U_n are potential functions independent of κ . Hence at points on S, V_1 and U_1 must satisfy the boundary conditions,

$$V_1 = U_1,$$

$$\frac{\partial V_1}{\partial n} - \frac{\partial U_1}{\partial n} = 4\pi \frac{\partial V_0}{\partial n}.$$

It follows that V_1 and U_1 are the values of the potential, outside and inside S respectively, due to a surface layer of density $-\partial V_0/\partial n = H_0^{(n)}$, the component of the applied field \mathbf{H}_0 along the outward-drawn normal to S . Now to the first order of approximation κV_1 and κU_1 are the values of the potential due to the induced magnetization. Hence the induced magnetization is equivalent to a surface layer of density $\kappa H_0^{(n)}$.

(b) Let \mathbf{I} be the intensity of the induced magnetization at a point Q in the body, and let R be the distance from Q to an external field point P . Then the corresponding potential V is given by

$$V = \int \mathbf{I} \cdot \text{grad} \frac{1}{R} dv,$$

the differentiation implied in the operator "grad" being with respect to the co-ordinates of Q and the integral being taken throughout the volume occupied by the body. Now

$$\mathbf{I} \cdot \text{grad} \frac{1}{R} = \text{div} \left\{ \frac{\mathbf{I}}{R} \right\} - \frac{1}{R} \text{div} \mathbf{I}$$

and

$$\text{div} \mathbf{I} = \text{div} (\kappa \mathbf{H}) = 0,$$

\mathbf{H} being the total intensity of the magnetic field at Q . Hence

$$\begin{aligned} V &= \int \operatorname{div} \left\{ \frac{\mathbf{I}}{R} \right\} dv = \int \frac{\mathbf{I}}{R} I^{(n)} dS \\ &= \int \frac{\kappa}{R} H^{(n)} dS, \end{aligned}$$

the (n) denoting the normal component and the integrals now being taken over the surface of the body.

The corresponding magnetic intensity due to the induced magnetization is

$$\mathbf{H} - \mathbf{H}_0 = \kappa \int \frac{H^{(n)}}{R^3} \mathbf{R} dS,$$

where \mathbf{R} is the vector drawn from Q on S to the field point P . The accurate expression for the equivalent surface density σ of the induced magnetization is therefore given by

$$\sigma = \kappa H^{(n)} = \kappa H_0^{(n)} + \kappa^2 \int \frac{H^{(n)} R^{(n)}}{R^3} dS \quad \dots\dots(2.1),$$

by the preceding equation. The second term here gives the error in the approximate formula $\sigma \doteq \kappa H_0^{(n)}$. It is equal to the normal intensity due to a surface layer of density $\kappa^2 H^{(n)}$ and hence its order of magnitude is $2\pi\kappa^2 H^{(n)}$ or $2\pi\kappa^2 H_0^{(n)}$.

§ 3. THE MECHANICAL FORCES

Since the induced magnetization is equivalent to a surface layer of density $\sigma \doteq \kappa H_0^{(n)}$, the mechanical forces on the magnetizable body are clearly equivalent to a surface distribution of force of an intensity per unit area equal to

$$\sigma \mathbf{H}_0 \doteq \kappa H_0^{(n)} \mathbf{H}_0 \quad \dots\dots(3.1).$$

In most practical cases part of the applied field \mathbf{H}_0 will consist of the magnetic field of the earth, say \mathbf{E}_0 , and it is easily seen that, although the earth's field is sensibly uniform throughout the dimensions of laboratory apparatus, its effect is by no means negligible. For if

$$\mathbf{H}_0 = \mathbf{E}_0 + \mathbf{F}_0,$$

the resultant force on the body is

$$\kappa \int H_0^{(n)} \mathbf{H}_0 dS = \kappa \mathbf{E}_0 \int H_0^{(n)} dS + \kappa \int H_0^{(n)} \mathbf{F}_0 dS.$$

But

$$\int H_0^{(n)} dS = 0.$$

Hence the force is

$$\kappa \int \mathbf{F}_0^{(n)} \mathbf{F}_0 dS + \kappa \int \mathbf{E}_0^{(n)} \mathbf{F}_0 dS \quad \dots\dots(3.2),$$

i.e. it is simply the sum of the forces exerted by the field \mathbf{F}_0 on the induced magnetization due to the earth's field \mathbf{E}_0 and on the induced magnetization due to the field \mathbf{F}_0 .

In Rankine's method it is more convenient to measure the mechanical force exerted on the magnet producing the field, rather than the force exerted on the magnetizable body, but here again it is necessary to allow for the effect of the earth's

field. Clearly the force exerted on the magnet by the body is equal and opposite to the force exerted on the body by the magnet, and this latter is

$$\begin{aligned}\int \sigma \mathbf{F}_0 dS &= \kappa \int H_0^{(n)} \mathbf{F}_0 dS \\ &= \kappa \int F_0^{(n)} \mathbf{F}_0 dS + \kappa \int E_0^{(n)} \mathbf{F}_0 dS,\end{aligned}$$

i.e. the same result as before is obtained. Although the second term, due to the earth's field, is in general not zero, it can be made to vanish in the experimental arrangement adopted by Rankine, as is shown below.

The simplest general case arises where the applied field is due to a magnetic pole of strength m placed very near to the body. In these circumstances the surface of the body can be regarded as an infinite plane. If the shortest distance of the pole from the body is p , the distance r in a direction making an angle θ with the shortest distance is $p \sec \theta$. The equivalent surface density σ at the point (r, θ) is given by

$$\sigma = \kappa (m/r^2) \cos \theta + \kappa E_0^{(n)},$$

allowing for the component of the earth's field normal to the surface. Hence the resultant attraction on the body or on the pole is

$$\int \sigma (m/r^2) \cos \theta dS,$$

where

$$\begin{aligned}dS &= d[\pi (p \tan \theta)^2] \\ &= 2\pi p^2 \tan \theta \sec^2 \theta d\theta.\end{aligned}$$

Hence the resultant attraction is

$$(\pi \kappa m^2 / 2p^2) + 2\pi \kappa m E_0^{(n)} \dots (3.3).$$

The presence of the second term involving $E_0^{(n)}$ illustrates the general conclusion reached in the last paragraph.

In the case considered by Rankine the magnetic pole S is at a horizontal distance c from the centre of a magnetizable sphere of centre C and radius a . The other pole N of the magnet is vertically below S and exerts a negligible effect. Neglecting at first the effect of the earth's field, the attractive force on the magnetic pole can be calculated as follows:

If a straight line SP_1P_2 is drawn through S making an angle θ with SC , it will meet the surface of the sphere at points P_1 and P_2 at distances R_1 and R_2 from S where

$$R_1 R_2 = c^2 - a^2$$

and

$$\frac{1}{2} (R_1 + R_2) = c \cos \theta.$$

At P_1 and P_2 , $H_0 = m/R_1^2$ and m/R_2^2 and the values of the surface density σ are $-\kappa m \cos \psi / R_1^2$ and $+\kappa m \cos \psi / R_2^2$ respectively, ψ being the angle between the normals to the sphere at P_1 , P_2 and the line SP_1P_2 . Hence the induced pole-strengths on surface elements dS_1 and dS_2 at P_1 and P_2 are respectively

$$-\kappa m \cos \psi dS_1 / R_1^2 \quad \text{and} \quad +\kappa m \cos \psi dS_2 / R_2^2,$$

i.e. $\kappa m d\omega_1$ and $\kappa m d\omega_2$, where $d\omega_1$ and $d\omega_2$ are the solid angles subtended at S by dS_1 and dS_2 . The mechanical forces on these elements of area parallel to SC are therefore

$$\kappa m^2 \cos \theta d\omega_1 / R_1^2 \quad \text{and} \quad \kappa m^2 \cos \theta d\omega_2 / R_2^2.$$

E_* is the component in the parallel direction. If the component of the earth's field along SC is E_* the additional attraction will be

$$\frac{4}{3}\pi a^3 \kappa E_* \cdot \frac{2m}{c^3} = \frac{8}{3}\pi \kappa m E_* s^3 \quad \dots\dots(3.5),$$

since the effective component of the magnetic doublet is in the end-on position.

Taking the figures given by Rankine, viz.

$$c = 1.80 \text{ cm.}, \quad a = 1.28 \text{ cm.}, \quad m = 50 \text{ c.g.s. units},$$

and taking E_* to be 0.16 gauss, we have for the uncorrected value of the attraction

$$F = 8.48 \times 10^3 \kappa \text{ dynes},$$

and the correction due to the earth's field is

$$F_* = 24\kappa \text{ dynes},$$

which amounts to less than $\frac{1}{3}$ per cent. Of course the correction can be reduced to zero by orienting the apparatus so that the line SC is perpendicular to the magnetic meridian.

§ 4. THE FORCE DUE TO DISTRIBUTED POLES

The poles of a bar magnet are not concentrated in two definite points but are distributed throughout the length of the magnet, and it is therefore necessary to correct Rankine's formula so as to allow for the spatial distribution of the poles. In the experimental arrangement adopted by Rankine the bar magnet was cylindrical, its axis was vertical, the centre C of the paramagnetic sphere was on a level with one end of the bar magnet, and the resultant horizontal force on the sphere was measured with a torsion balance. The poles of the magnet may be regarded as distributed along its axis, and it seems to be impossible to obtain any simple expression for the horizontal force unless the distance of the magnet from the surface of the sphere is large compared with the distance over which the poles are distributed. In these circumstances the force of attraction would be extremely small. If, however, the axis of the magnet is horizontal and passes through the centre of the sphere when produced, the problem becomes considerably simplified. It seems worth while to carry out the necessary calculations in this case as there is some hope that, with this modification of the experimental arrangement, Rankine's method may yield *absolute* values of susceptibility.

r, θ, ϕ It is convenient to use spherical polar co-ordinates (r, θ, ϕ) with the origin at the centre C of the paramagnetic sphere and the axis coinciding with the axis of the bar magnet. The potential due to a unit pole on the axis at a distance ζ from C is

$$(r^2 + \zeta^2 - 2r\zeta \cos \theta)^{-\frac{1}{2}} = \zeta^{-1} \sum_{n=0}^{\infty} (r/\zeta)^n P_n(\cos \theta), \quad (r < \zeta),$$

$m(\zeta)$ where $P_n(\cos \theta)$ is Legendre's function of order n . Hence, if the linear density of the pole strength is $m(\zeta)$, the potential V_0 of the applied field is given by

$$V_0 = \sum_{n=0}^{\infty} c_n r^n P_n(\cos \theta),$$

c_n where

$$c_n = \int \zeta^{-n-1} m(\zeta) d\zeta \quad \dots\dots(4.1).$$

The component of the applied field normal to the surface of the sphere is given by

$$\begin{aligned} H_0^{(n)} &= -(\partial V / \partial r)_{r=a} \\ &= - \sum_{n=0}^{\infty} n c_n a^{n-1} P_n(\cos \theta), \end{aligned}$$

and the component parallel to the axis is given by

$$\begin{aligned} H_0^{(z)} &= -(\partial V / \partial z)_{r=a} \\ &= \{-\cos \theta (\partial V / \partial r) + \sin \theta (\partial V / r \partial \theta)\}_{r=a}. \end{aligned}$$

$$\begin{aligned} \text{Now } \left\{ -\cos \theta \frac{\partial}{\partial r} + \sin \theta \frac{\partial}{r \partial \theta} \right\} r^m P_m(\cos \theta) \\ = r^{m-1} \{-m \cos \theta P_m(\cos \theta) + \sin \theta \partial P_m(\cos \theta) / \partial \theta\} \\ = m r^{m-1} P_{m-1}(\cos \theta), \end{aligned}$$

in virtue of one of the standard recurrence formulae. Hence

$$H_0^{(z)} = - \sum_{m=1}^{\infty} m c_m a^{m-1} P_{m-1}(\cos \theta).$$

The total mechanical force on the sphere is

$$\begin{aligned} \kappa \int H_0^{(n)} H_0^{(z)} dS &= 2\pi\kappa \int_0^\pi \sum_{n,n} m n c_m c_n a^{m+n} P_{m-1}(\cos \theta) P_n(\cos \theta) \sin \theta d\theta \\ &= 4\pi\kappa \sum_{n=1}^{\infty} \frac{n(n+1)}{2n+1} c_n c_{n+1} a^{2n+1} \dots\dots (4.2). \end{aligned}$$

For a unit pole at a distance c from the origin

$$c_n = c^{-n-1},$$

and the expression for the force becomes

$$\frac{4\pi\kappa}{c^2} \sum_{n=1}^{\infty} \frac{n(n+1)}{2n+1} s^{2n+1},$$

where $s = a/c$. It may be verified that this is the expression in powers of s of the function

$$\begin{aligned} F(s) &= \frac{\pi\kappa}{4c^2} \left\{ \frac{4s(1+s^2)}{(1-s^2)^2} - 2 \log \frac{1+s}{1-s} \right\} \\ &= \frac{\pi\kappa}{4c^2} (\sinh 2y - 2y), \quad (s = \tanh \frac{1}{2}y), \end{aligned}$$

which appears in Rankine's formula (3.4).

In general it will be necessary to determine $m(\zeta)$, the linear density of the pole-strength, by experiment and to calculate the coefficients c_n (4.1), by numerical integration. The rapidity of the convergence of the series (4.2) given above for the total mechanical force can be estimated as follows. If the nearest point on the bar magnet is at a distance c from the origin then

$$c_n = \int \zeta^{-n-1} m(\zeta) d\zeta < m/c^{n+1},$$

where m is the total pole-strength. Now the n th term of the series is

$$\frac{n(n+1)}{2n+1} c_n c_{n+1} a^{2n+1} < \frac{m^2 a}{2c^3} (n+1) s^{2n}$$

where $s = a/c$. Hence the series converges at least as rapidly as the series

$$\sum_{n=1}^{\infty} (n+1) s^{2n} = (1-s^2)^{-2} - 1 \quad \dots\dots(4.3).$$

p Now the remainder after p terms of the series (4.3) is

$$R_p = \sum_{n=p+1}^{\infty} (n+1) s^{2n} = \frac{s^{2p+4}}{(1-s^2)^2} + (p+2) \frac{s^{2p+2}}{(1-s^2)} \quad \dots\dots(4.4),$$

and the remainder after p terms of the series (4.2) cannot exceed this number. Taking, for example, the value of s used by Rankine,

$$s = 0.711, \quad s^2 \doteq \frac{1}{2}, \\ (1-s^2)^{-2} - 1 \doteq 3 \quad \text{and} \quad R_{10} \doteq 0.0127.$$

Thus the error involved in neglecting all terms after the 10th is less than 0.42 per cent. The preceding analysis appears to furnish the necessary correction for the finite spread of the poles, and to furnish it in a form which does not require too laborious a series of calculations.

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Finally, the author wishes to express his gratitude to Prof. Rankine for his continued interest and helpful criticism.

REFERENCE

- (1) RANKINE. *Proc. phys. Soc.* **46**, 391 (1934).

THE RELATION BETWEEN THE APPARENT INTENSITY OF A BEAM OF LIGHT AND THE ANGLE AT WHICH THE BEAM STRIKES THE RETINA

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ABSTRACT. Stiles and Crawford recently observed that the efficiency of a pencil of light was much greater when it passed through the centre of the lens of the eye than when it traversed an outer segment. This result has been confirmed for three observers by use of the authors' subjective photometer, in which a method of binocular matching is employed. One or two suggestions as to the origin of the phenomenon are put forward; it is almost certainly associated with the angle of incidence of the light on the retina, which may have an inherent directional sensitivity.

§ 1. INTRODUCTION

STILES and Crawford⁽¹⁾ showed recently that when a narrow pencil of light was transmitted through the pupil of the eye and came to a focus on the retina, the brightness of the patch varied according to the part of the pupil used. When the light was axial the brightness was a maximum, but as the distance from

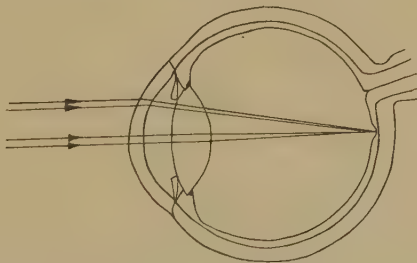


Figure 1. Cross-section of the eye, showing the path of an axial and an extra-axial pencil of light, each coming to a focus on the fovea.

the centre of the iris was increased the apparent brightness diminished. It can be seen at once from figure 1 that the axial beam corresponds to light incident normally on the retina, when the patch is being viewed on the fovea and the small eccentricity of the latter is neglected; while with the extra-axial beam, the greater the distance from the centre the more obliquely does the light strike the retina.

Stiles and Crawford obtained their results by a method of flicker photometry in which the reference beam was transmitted centrally through the pupil of the eye, and the test beam at various distances from the centre of the same eye. In the present case a different type of apparatus was available which, although not capable of the same accuracy as that used by Stiles and Crawford, gave a confirmatory set of curves which seemed worthy of publication.

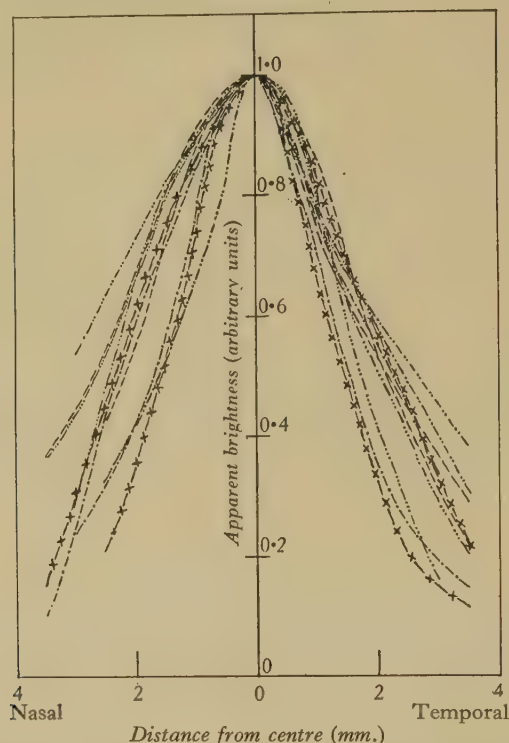


Figure 2. Curves showing relation between brightness of a beam of light and the distance from the centre of the iris at which the pencil enters the eye. Observer: W.D.W. Right eye.

White -----, Red - · - · - · -, Yellow · · · · ·, Green - - - - - , Blue - x - x - x -.

§ 2. APPARATUS

The authors' subjective photometer, described elsewhere⁽²⁾, was used to give the curves shown below. The instrument depends on a method of binocular matching in which a patch seen by the left eye is compared with a patch seen by the right eye. The left patch thus acts as a reference standard when the part of the pupil used in the right eye is varied.

§ 3. CONDITIONS OF OBSERVATION

Both eyes were dark-adapted for about 20 minutes before the observations were made, and comparison between the patches was made instantaneously and not by gazing continuously at the light. The diameter of the beam at the point where

it entered the eye was about 0.040 in., and the angular subtense of each patch seen on the retina was approximately $1\frac{1}{2}^\circ \times 3^\circ$. Only a horizontal traverse of the observer's pupil was possible. No attempt was made to increase the diameter of the pupil by the use of mydriatics.

§ 4. RESULTS

Observations were made by Dr R. J. Lythgoe and by the authors. Data for both white light corresponding to a colour temperature of about 2800° K., and colours selected by means of Ilford's spectrum filters, were obtained and the results

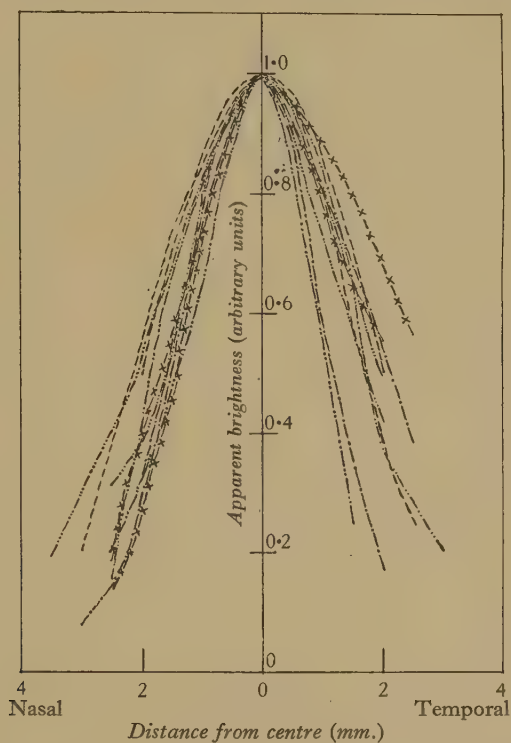


Figure 3. Curves showing relation between brightness of a beam of light and the distance from the centre of the iris at which the pencil enters the eye. Observer: J.H.N. Right eye.

White -----, Red - · - · - · -, Yellow · · · · ·, Green - - - - -, Blue - x - x - x -.

are shown in figures 2 to 4. The accuracy of observation was not high, the uncertainty of setting being of the order of 20 per cent. The spreading of the curves in figures 2 and 3, which include repeat observations, indicate the general reliability of the data.

§ 5. CONCLUSIONS

The mean curves for J.H.N., R.J.L., and W.D.W., figure 5, agree well with the data of Stiles and Crawford. These mean curves have been plotted in relation to the angle of incidence of the light on the retina, the angle being derived from the dimensions of an average eye. The magnitude of the effect is very striking and it is

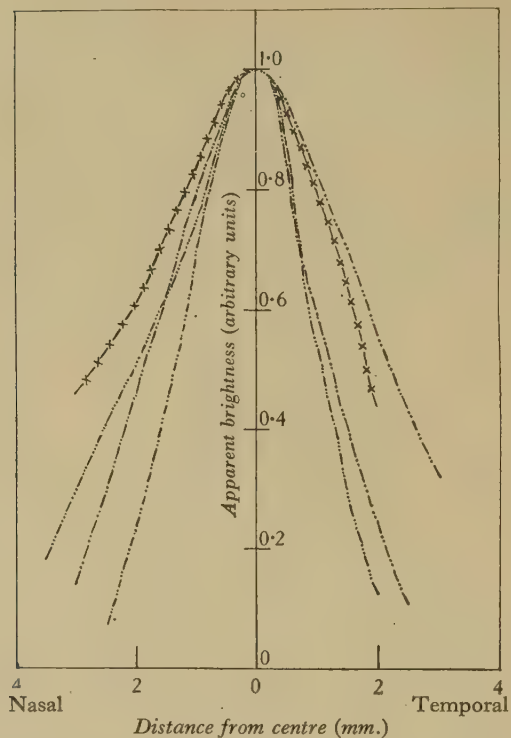


Figure 4. Curves showing relation between brightness of a beam of light and the distance from the centre of the iris at which the pencil enters the eye. Observer: R.J.L. Right eye.

Yellow -----. Green Blue -x-x-x-x-.

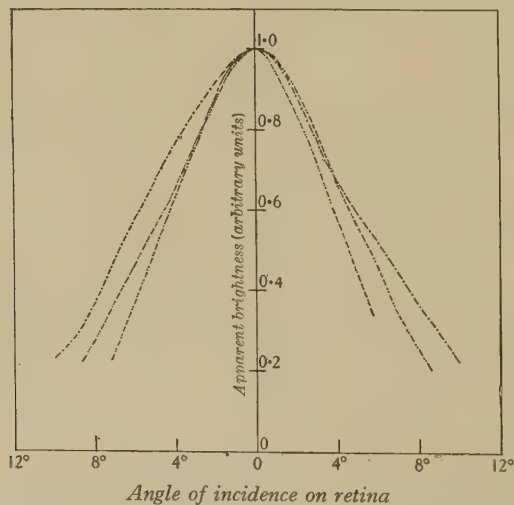


Figure 5. Mean curves showing the relation between the apparent intensity of a beam of light and the angle at which the beam strikes the retina.

W.D.W. -----. J.H.N. R.J.L. -x-x-x-x-.

obvious that the loss of brightness cannot be due to any absorption in the optical media of the eye. The most plausible suggestion put forward by Stiles and Crawford was that absorption took place in the pigment epithelium assumed to have migrated between the rods and cones, and that this absorption varied according to the angle of incidence, since the light would have to pass through varying thicknesses of the pigment.

While this may be the true explanation, it is not, as Stiles and Crawford admit, very convincing. In view of the structure of the retina, it seems to us that the sensitive membrane may very well have a fundamental directional sensitivity. It may be, for instance, that the light has to enter directly into a cone in order to produce a photochemical reaction. The irregular orientation of the cones might then explain the curves obtained. Alternatively the light may be totally reflected inside the walls of the cone, and when the angle of incidence becomes too great the light escapes outside the cell and is inactive. These suggestions are only guesses, but they illustrate the possibility that the phenomenon may be the result of a fundamental process in the retina.

§ 6. ACKNOWLEDGMENTS

We should like to express our thanks to Dr Lythgoe for his assistance in making some of the observations and to the Medical Research Council for their financial support.

REFERENCES

- (1) STILES, W. S. and CRAWFORD, B. H. *Proc. roy. Soc.* **112** (1933).
- (2) WRIGHT, W. D. and NELSON, J. H. *J. Sci. Instrum.* (Dec. 1935).

THE USE OF THERMOCOUPLES FOR PSYCHROMETRIC PURPOSES

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ABSTRACT. The paper deals with certain factors affecting the use of thermocouples for psychrometric purposes, and considers some of the advantages possessed by instruments of this type. An investigation is made for the purpose of determining the manner in which the wet-bulb depression depends on the degree of ventilation, the diameter of the wire, the thickness and length of the water film covering the junction of the wet thermocouple, and the relative positions of the wet and dry thermocouples. It is shown that the need for forced ventilation of the wet thermocouple decreases as the diameter of the wetted wire is diminished. A typical example is given showing that for a psychrometer composed of nichrome and constantan wires of 40 s.w.g. mounted in a still air enclosure, the percentage relative humidity derived from its readings is only two or three units greater than that given by a fully ventilated instrument, when psychrometric tables appropriate to the latter condition are used in each instance.

§ 1. INTRODUCTION

IN the course of some experiments in which very fine thermocouples were used to measure the distribution of vapour pressure in air streaming over a wet surface, it was found that relatively low air-velocities were sufficient to give the maximum depression of the wet bulb, and that in the complete absence of forced ventilation the depression of the wet bulb was within a few per cent of this maximum depression. It is clear that the diminished importance of adequate ventilation gives thermocouple psychrometers a great advantage over mercury-in-glass wet and dry thermometers. The necessary observations can also be obtained more quickly when thermocouples are used to measure humidities than when the dew-point method is employed, and the fact that smaller convection currents are set up is a further advantage in experiments where undisturbed air conditions are required.

The above experiments were first made early in 1933, but a subsequent search of the literature revealed that a few months earlier mention had been made elsewhere of the small amount of ventilation required by thermocouple psychrometers. References to these papers are included in the next section. The present paper deals with several factors which become of importance in the application of thermoelectric methods for psychrometric purposes.

§2. PRIOR REFERENCES TO THERMOCOUPLE PSYCHROMETERS

In 1929 E. Griffiths, J. R. Vickery and N. E. Holmes⁽¹⁾ used a psychrometer consisting of thirty-three wet and dry copper-constantan thermocouples connected in series, as a means of observing from a distance the relatively small wet-bulb depressions obtained in cold-storage holds on board ship. The wet junctions were each fitted with a muslin sleeve, comparable in size with the bulb of a clinical thermometer, and in consequence an air-speed of the order of 3 metres per second was needed to give the maximum depression.

M. Okada⁽²⁾, in making a study of air circulation in cold-storage warehouses, used thermocouples to measure the distributions of both temperature and humidity set up in a rectangular chamber cooled above and heated below. J. H. Lanning⁽³⁾ records the use of wet and dry copper-constantan thermocouples to measure the relative humidity in desiccators, the smallness of the quantity of water vapour introduced into the enclosure being considered an advantage.

R. Hilpert⁽⁴⁾, in his experimental determination of the evaporation and heat-transfer from a vertical plate in still air, used a manganin-constantan thermocouple of 0.15 mm. wire to measure the humidity of the air. The wet and dry thermocouples, surrounded by radiation shields, were mounted in a tube through which a slow stream of air passed before entering the experimental enclosure. The wet junction could be moistened as required by water forced from a small capillary tube by heating air in a closed upper space. Hilpert studied the effect of air-velocity on the depression of this psychrometer, and gives a curve showing the maximum depression to be produced by a velocity of only 20 cm./sec.

At about the same time H. Wald⁽⁵⁾ and L. Kettneracker⁽⁶⁾ also advocated the use of very fine wire thermocouples as a means of reducing the necessity for artificial ventilation, and published similar theoretical support. V. Rossi⁽⁷⁾ has employed thermocouples in a study of the temperature and humidity gradients in the atmosphere, whilst K. Schropp⁽⁸⁾ has recently employed this means of measuring humidities in an experimental investigation of the factors governing the formation of frost and dew on cooling tubes.

E. J. Blades⁽⁹⁾ has used an analogous method for the determination of the vapour pressure of a solution, the sample being in the form of a drop and retained in a loop formed at the junction of a thermocouple composed of very fine wires.

§3. THEORY DUE TO KETTERNACKER

Kettneracker derives the following expression for the ratio of the observed to the maximum difference in temperature between the wet and dry thermometers, on the assumption that the Joule heat developed within the wire and the radiation thereto can be neglected:

$$a = \frac{(T_a - T_0)}{(T_a - T_w)} = 1 / \left\{ 1 + \frac{\pi}{2} \sqrt{(\alpha_D d^3)} (\sqrt{\lambda_1} + \sqrt{\lambda_2}) / \alpha F \left[1 + \frac{r}{C_p} \left(\frac{dx}{dT} \right)_{T=T_w} \right] \right\}, \quad a$$

where T_a is the dry-bulb temperature, T_0 the observed wet-bulb temperature,

T_w the fully ventilated wet-bulb temperature, d the diameter of the wire, λ_1 and λ_2 are the thermal conductivities of the metals composing the wires, α_D is the surface emissivity of the wire, F the area of the moist surface, r the latent heat of vaporization of water, C_p the specific heat of air, α the coefficient of heat-transfer from air to surface, and $(dx/dT)_{T=T_w}$ the change in saturated water-content of the air with change of temperature at T_w .

The tables for use with a fully ventilated wet-and-dry-bulb thermometer can be used to give the true relative humidity from readings obtained with a thermocouple psychrometer when the value of a is unity. It will be seen that in the foregoing expression a tends towards this value as α is increased, as the thermal conductivity of the wire is decreased, and as the diameter approaches zero. In the usual type of psychrometer α is increased by means of forced ventilation, but since α also increases as the diameter decreases, the foregoing equation shows clearly that the need for forced ventilation becomes less as the diameter of the wire is decreased.

§ 4. DESCRIPTION OF EXPERIMENTS

Selection of thermocouple elements. The metals chosen for the two thermocouple elements were nichrome and constantan, which in the neighbourhood of room-temperature have a somewhat greater e.m.f. per degree than the copper-constantan combination more frequently employed, and further possess relatively low thermal conductivities, that of nichrome being about 0.03 c.g.s. unit and that of constantan being 0.06 c.g.s. unit.

Comparison between thermocouples and mercury thermometers. Two thermocouples were made up of 40-gauge nichrome and constantan wires joined end to end. In order to retain the moisture on the wet thermocouple the wire of this thermocouple was wrapped with very fine cotton for a distance of about a centimetre on each side of the junction. These thermocouples were mounted in a wind tunnel in which ordinary wet and dry mercury-in-glass thermometers were also suspended. Observations of the wet-bulb depressions were made on both types of psychrometer, and also on a fully ventilated Assmann psychrometer, and the values of a were determined for the unventilated condition and for wind speeds of 65 and 260 cm./sec. The values of a for these three air conditions were 0.80, 0.95 and 0.99 for the mercury thermometers, and 0.97, 0.99₅ and 1.00 for the thermocouples. This result shows clearly that the provision of forced ventilation is of far less importance when fine wire thermocouples are used than in the case of mercury-in-glass thermometers.

The thermocouple psychrometer possesses the further advantage that it reaches its equilibrium temperature in a few seconds, whereas the wet thermometer takes several minutes.

Tests with thermocouples of various diameters. A number of thermocouples were prepared, by using nichrome and constantan wires of 14, 18, 26, 32 and 40 s.w.g., the two elements being butt-welded together. A covering of fine cotton was wrapped over each thermocouple so as to extend for a distance of 5 cm. on each side of the

junction of the two wires. Observations were made of the wet-bulb temperature indicated by each of these thermocouples in the absence of forced ventilation, and in a draught sufficient to produce the maximum depression of the wet bulb. The former condition is referred to in this paper by the designation "still air". The results obtained are set out in table 1, a being the ratio of the still-air depression to the maximum depression. The air-temperature was approximately $18^{\circ}\text{C}.$, and the relative humidity varied from 35 to 40 per cent.

Table 1. Results obtained with thermocouples of various diameters

Wire gauge (s.w.g.)	Diameter of wire (cm.)	Depression in still air ($^{\circ}\text{C}.$)	Maximum depression ($^{\circ}\text{C}.$)	a
14	0.202	6.35	7.20	0.88
18	0.12	7.15	7.85	0.91
—	—	5.28	5.86	0.90
26	0.045	5.80	6.15	0.94 ₃
32	0.028	6.62	6.89	0.95 ₇
40	0.017*	5.81	6.02	0.96 ₃
40	0.012	6.00	6.10	0.98 ₄

* Wires doubled back and twisted together.

The true wet-bulb reading is given when $a = 1$, and it is seen from figure 1 that the departure from this value is proportional to the square root of the diameter

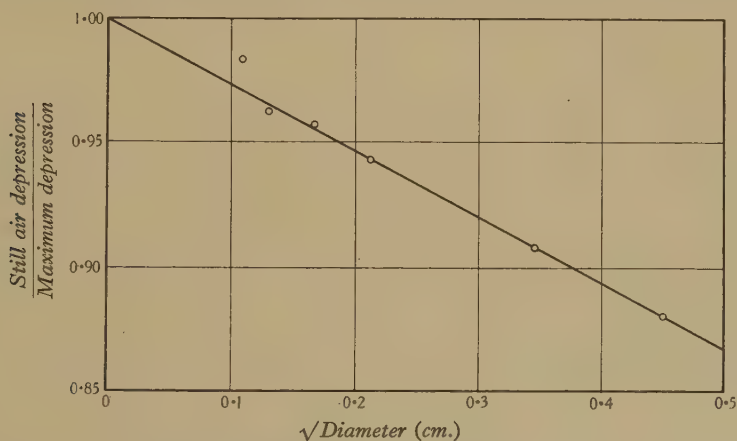


Figure 1. $\frac{\text{Still air depression}}{\text{Maximum depression}}$, against square root of diameter of wire.

of the wire. This result is indicated by Ketternacker's theory, if α is assumed to be independent of the diameter. This agreement is presumably fortuitous, since α , the coefficient of heat-transfer, is known to increase rapidly as the diameter diminishes.

Investigation into the effect of the thickness of the cotton covering. A few measurements have been made for the purpose of showing the extent to which the depression of the wet thermocouple is dependent on the thickness of the cotton covering.

A number of 40-gauge thermocouples were prepared having their junctions covered with cotton of various thicknesses, and were tested in a manner similar to that already described. The results obtained are set out in table 2, from which it will be seen that value of a decreases in an approximately linear manner with increase in cotton-thickness.

Table 2. Results obtained with cotton coverings of various thicknesses

Thickness of cotton (cm.)	Depression in still air ($^{\circ}\text{C}.$)	Maximum depression ($^{\circ}\text{C}.$)	a
0.045	7.50	7.93	0.94 ₆
0.024	7.62	7.93	0.96 ₁
0.010	5.58	5.79	0.96 ₃
0.009	7.73	7.98	0.96 ₉
0.007	7.65	7.87	0.97 ₂
0.0015	7.70	7.86	0.98 ₀

The influence of the length of cotton covering on the wet-bulb depression. Tests of a similar kind were carried out to ascertain how the wet-bulb depression depended on the length of wire that was covered by cotton and thus kept wet. The cotton covering was wound to equal distances on each side of the junction, and two sizes of wire were examined in this way, namely the 26 and 18 s.w.g. It will be seen from the results plotted in figure 2 that total coverings extending over a length of at

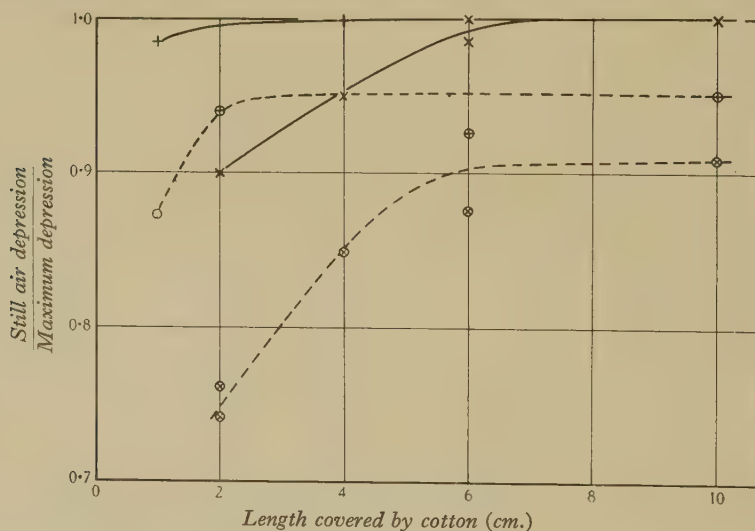


Figure 2. Influence of cotton covering on a . \otimes 18 s.w.g. still air; \times 18 s.w.g. air speed 250 cm./sec.; \oplus 26 s.w.g. still air; $+$ 26 s.w.g. air speed 250 cm./sec.

least 3 and 6 cm. are required in these respective cases to ensure the maximum values of a being reached. For 40-gauge wire a wrapping over a length of about 1 cm. appeared to be sufficient, but results with shorter lengths were not obtained.

It will be observed from the curves in the figure that when the length of wetted wire was less than the above value even the maximum degree of ventilation used in

these experiments was insufficient to give a a value of unity. It would appear from this that unless the wire is wetted for a sufficient length on both sides of the junction, even strong ventilation does not lead to true values for the relative humidity. A similar result would probably hold good for any form of wet-bulb thermometer.

Calibration of a thermocouple psychrometer for use in an unventilated enclosure. It has already been shown that provided the wet thermocouple is composed of very thin wires the relative humidity deduced from its depression in still air is within a few per cent of the true humidity. The calibration of such a thermocouple psychrometer, which has been used for the measurement of the relative humidity of a closed chamber, will now be described.

This psychrometer was constructed from 40-gauge wires, and consisted of wet and dry thermocouples differentially connected together and a separate dry thermocouple. The instrument was mounted in a closed chamber, the two dry thermocouple junctions being alongside each other and in a position where they were not influenced by the cooler wet thermocouple. The relative humidity of the air in the chamber was varied from about 20 per cent to saturation, and readings were observed of the dry temperature and depression of the wet bulb, as given by the differential thermocouple, both when the air-movement was due to natural convection only, and when the air was vigorously stirred by means of a fan driven by an external motor. This forced ventilation was sufficient to give the maximum depression of the wet thermocouple, and by comparing these values with those obtained in the absence of ventilation a calibration for the latter condition is obtained.

The results are given in table 3, psychrometer tables compiled for an adequately ventilated instrument being used for both ventilated and unventilated conditions.

Table 3. Relative humidities given by thermocouple psychrometer when unventilated and when fully ventilated

Dry-bulb reading (°C.)	Wet-bulb reading		a	Relative humidity	
	fully ventilated (°C.)	un- ventilated (°C.)		true (per cent)	un- ventilated (per cent)
22·00	10·93	11·30	0·97	21	24
21·74	11·37	11·78	0·96	25	28
21·72	11·90	12·38	0·95	29	32
20·98	11·26	11·70	0·94	28	30
20·82	13·26	13·70	0·94	41·5	45
20·37	15·55	15·82	0·94	61	62·5
20·68	17·10	17·35	0·93	70	72
20·72	18·50	18·70	0·88	81	83
21·12	20·20	20·43	0·75	92	94
22·02	21·64	21·75	0·72	97	97·5

It will be seen that the values of a are somewhat smaller than those previously given for wire of this size. The still-air values in the latter case had been obtained in an open-ended wind tunnel situated in a large room, and it is probable that

there was relatively more air-movement in this instance than in the closed chamber used in the present tests. Over the greater part of the humidity-range, however, the values obtained for the relative humidity from the readings of the unventilated instrument are only some two or three units too great.



Figure 3. Isothermals around a wet horizontal thermocouple in still air. Humidity 52 per cent. Dry thermocouple reading decreased by \odot , 0°C .; Δ , 0.6°C .; $+$, 1.2°C .; \times , 2.4°C .; $*$, 3.6°C . Depression of wet thermocouple, 6.1°C .

Considerations regarding the location and requisite distance apart of the wet and dry thermocouples. One advantage which the thermocouple psychrometer possesses over hygrometers of other types is that its small size permits local variations in humidity to be studied. In making such a determination, the two temperature-measurements should be made in positions as close together as is consistent with avoidance of the errors likely to arise from mutual interference of the thermocouple readings. When the humidity is being determined by a ventilated thermocouple

psychrometer the wet and dry thermocouples need not be more than a millimetre or two apart, provided that the dry thermocouple is situated to windward of the wet thermocouple.

In unventilated conditions a separation of about ten times this distance is essential to prevent the dry-bulb reading from being influenced by the cool air surrounding the wet bulb. Figure 3 indicates the extent to which the reading of the dry thermocouple is lowered, when this element is parallel to the wet thermocouple and at various distances above, below, or to either side of it. It will be observed that the effect of the stream of cold air falling from the wetted surface persists to a considerable distance, and care should be taken to ensure that the dry thermocouple shall not be placed within this region.

§ 5. ADVANTAGES AND APPLICATIONS OF THERMO- COUPLE PSYCHROMETERS

Apart from the present purposes for which thermocouple psychrometers have been found to be well suited, namely the measurement of the humidity-gradient above a moist surface either with or without forced ventilation, and as an alternative to the dew-point method of determining the humidity of a still-air enclosure, this type of instrument possesses many other possible spheres of application. When, for instance, the air under test is very dry, the large amount of cooling required by a dew-point thimble before the dew point is attained makes the determination by this means laborious, and thermocouples may be preferred. The rapidity of the response of a thermocouple, which permits fluctuations in humidity to be detected, has already been mentioned. This type of psychrometer also possesses the normal advantages of the thermoelectric methods in that the instrument is distant-reading, and can easily be made recording. It could also readily be adapted as a method of humidity-control by the employment of some such device as that suggested by R. M. Zabel and R. R. Hancox⁽¹⁰⁾, in connexion with the use of thermocouples as a means of controlling furnace-temperatures.

Multi-element thermocouples or those composed of elements with a large temperature coefficient of voltage would be of considerable service in vapour-pressure measurements in which a high sensitivity is required, for instance measurements near saturation or at low temperatures.

§ 6. ACKNOWLEDGMENTS

The above investigation formed part of an item of research conducted at the National Physical Laboratory on behalf of the Engineering Committee of the Food Investigation Board, and the author desires to express his thanks to this Committee for permission to publish an account of the results obtained. Acknowledgment is also made to Mr M. J. Hickman for assistance with the experimental work.

REFERENCES

- (1) GRIFFITHS, E., VICKERY, J. R. and HOLMES, N. E. *Spec. Rep. Food Invest. Bd*, Lond., No. 41, p. 34 (1932).
- (2) OKADA, M. *J. Imp. Fish. Inst.*, Tôkyô, **26**, No. 2 (March 1931).
- (3) LANNING, J. H. *Industr. Engng Chem.* (Analytical ed.), **4**, 286 (1932).
- (4) HILPERT, R. *Forschungsh. Ver. deutsch. Ing.* No. 355 (July-Aug. 1932).
- (5) WALD, H. *Z. ges. Kälteindustr.* **39**, 111 (1932).
- (6) KETTERNACKER, L. *Z. InstrumKde*, **52**, 319-24 (1932).
- (7) ROSSI, V. *Acta Soc. Sci. fenn.* **6**, 25, 1-22 (1932-3).
- (8) SCHROPP, K. *Z. ges. Kälteindustr.* **42**, 81-5, 126-31, 151-4 (1935).
- (9) BLADES, E. J. *J. sci. Instrum.* **11**, 223-5 (1934).
- (10) ZABEL, R. M. and HANCOX, R. R. *Rev. sci. Instrum.* **5**, 28-9 (1934).

THERMAL DIFFUSION IN DEUTERIUM MIXTURES

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ABSTRACT. With the object of comparing the molecular fields of hydrogen and deuterium, the thermal diffusion effects⁽¹⁾ in mixtures of hydrogen-nitrogen and of deuterium-nitrogen have been measured over a temperature-range -190° to $+100^{\circ}$ C. It appears that deuterium has the same type of field as hydrogen. Helium-nitrogen mixtures, which are of interest because the mass ratio is the same as in deuterium-nitrogen mixtures, were also examined.

§ 1. INTRODUCTION

MEASUREMENTS of thermal diffusion in gas mixtures have given information about the nature of molecular fields of force^(2,3). The amount of thermal separation due to a temperature-gradient from T_1 to T_2 is found, in accordance with Chapman's theory⁽¹⁾, to be generally proportional, except at low temperatures, to $\log(T_1/T_2)$; thus the separation may be expressed as $k_t \log(T_1/T_2)$. The ratio of the quantity k_t thus experimentally determined to the value $k_{t\infty}$ calculated for the particular case in which the molecules behave like rigid elastic spheres has been termed the *thermal separation ratio* R_t . If the molecules are point centres of force varying inversely as the q th power of the distance, then R_t may be regarded as an approximate measure of the index q . Values of q have been determined for many gases, and reasonable agreement with values deduced by other methods is found.

The method has now been applied to a comparison of the molecular fields of hydrogen and deuterium. It was convenient for this purpose to compare the thermal separation in a series of hydrogen-nitrogen and deuterium-nitrogen mixtures. Helium-nitrogen mixtures were also examined. These are interesting because helium has the same mass as deuterium but a different electronic structure; this is just the converse of the case of hydrogen and deuterium.

The experiments fall into two parts: (1) measurements of thermal separation in mixtures of varying proportions, two fixed temperatures being used; these are the room-temperature T_2 and the steam-temperature T_1 . From the experimental values of k_t and the theoretical values of k_t for rigid elastic spheres, the value of R_t over this temperature-range is calculated. (2) Measurements of thermal separation with varying temperature-differences. In this case T_1 is the room-temperature and T_2 varies from room-temperature down to -190° C.

 T_1, T_2 k_t $k_{t\infty}$ R_t q

It has previously been found⁽²⁾ that R_t for hydrogen-nitrogen mixtures is constant at temperatures above -80°C . but that at lower temperatures its value diminishes. This result has been interpreted as showing that a diminution in the index of the repulsive force occurs as the temperature decreases. It is of interest therefore to compare the extent of the change in R_t for deuterium-nitrogen mixtures with that in hydrogen-nitrogen mixtures.

§ 2. METHOD

Preparation of the deuterium. The deuterium was prepared by distilling in a vacuum about 0.2 cm^3 of heavy water on to clean sodium. Two samples were prepared: the first from water containing about 96 per cent of deuterium, the second from water containing 98 per cent.

A complication arises from the presence of HD and H_2 molecules. Sample 1 had a deuterium-content of 92 per cent, and consisted therefore of 84 per cent of D_2 , 15 per cent of HD, and 1 per cent of H_2 .^{*} Sample 2 had a deuterium-content of 96 per cent D_2 and 4 per cent HD. As a first approximation it is sufficient to regard the mixture of D_2 , HD, and H_2 as a simple gas whose molecular weight is the weighted mean of its constituents. Any thermal diffusion effect between these molecules themselves will certainly be too small to detect.

The separation measurements. The thermal separation was measured with apparatus essentially similar to that described in earlier papers.

For the first part of the work a steam-jacketed bulb with a capacity of about 4 cm^3 was attached to the katharometer, one cell of which thus formed the cold side at room-temperature. The factor for the conversion into total separation of the change in concentration measured by the katharometer was determined by means of separate experiments with common gas mixtures for which the experimental values of k_t were already known. The three sets of mixtures, $\text{H}_2\text{-N}_2$, $\text{D}_2\text{-N}_2$ and He-N_2 , were each examined over a wide range of concentration under identical conditions.

The measurements at low temperatures were made with the apparatus previously used for the rare gases⁽²⁾. The temperatures, however, were measured by a pentane thermometer instead of the thermocouple. The thermometer was checked against a similar thermometer calibrated at the Reichsanstalt.

§ 3. RESULTS

The variation of separation with concentration. Figure 1 shows the variation of separation with concentration when $\log_{10} (T_1/T_2) = 0.112$. Sample 1 of deuterium was used in this part of the work.

The thermal separation occurring in a mixture is a function of the mass, size and proportions of the two kinds of molecules as well as of the molecular fields. The thermal-separation ratio, however, depends only on the molecular forces, and it is this quantity which must be evaluated for a comparison of the fields of hydrogen

* For the analysis of the deuterium we are indebted to Dr Farkas.

and deuterium. It is defined as the ratio of k_t experimentally determined as $d(\text{separation})/d(\log T)$, to the value $k_{t\infty}$ calculated for molecules behaving like rigid elastic spheres. This calculated value is derived from Chapman's expression involving the masses, sizes and proportions of the two kinds of molecules. When numerical values for the mass and size are inserted, a comparatively simple expression for $k_{t\infty}$ in terms of the proportions is obtained. Such expressions have already

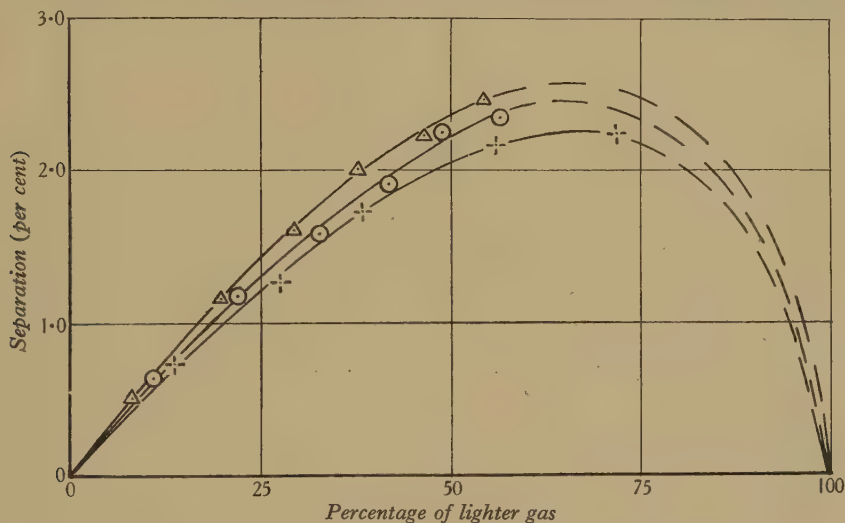


Figure 1. Variation of separation with concentration when $\log_{10} T_1/T_2 = 0.112$, $T_1 = 100^\circ \text{C.}$, and $T_2 = 14^\circ \text{C.}$ \odot $\text{H}_2\text{-N}_2$; $+$ $\text{D}_2\text{-N}_2$; \triangle He-N_2 .

been given for hydrogen-nitrogen and helium-nitrogen mixtures⁽²⁾. For deuterium-nitrogen the expression for k_t as calculated for rigid elastic spheres is as follows:

$$k_{t\infty} = \frac{5}{2} \frac{0.274n_1 + 0.286n_2}{1.817n_1/n_2 + 0.733n_2/n_1 + 2.667},$$

where n_1 is the proportion by volume of nitrogen, n_2 the proportion by volume of deuterium, and $n_1 + n_2 = 1$. In the calculation, the molecular diameter of deuterium was taken as being equal to that of hydrogen: the viscosity measurements of Cleave and Maass⁽⁵⁾, published while this work was in progress, show this to be justified. The above expression applies to pure deuterium of mass 4; a modification was necessary to take account of the slightly smaller *mean* mass of the deuterium sample 1.

The mean value of R_t over the range of concentrations examined was found to be as shown in table 1.

Table 1. Values of R_t and q

Mixture	R_t	q
$\text{H}_2\text{-N}_2$	0.59	11
$\text{D}_2\text{-N}_2$	0.58	11
He-N_2	0.65	12.5

The error in determining R_t is about 2 per cent. The difference between the values for hydrogen-nitrogen and deuterium-nitrogen is thus within the experi-

mental error, and we may conclude that at normal temperatures the deuterium molecule has a force-field similar to that of the hydrogen molecule.

R_t for the helium-nitrogen mixture is definitely greater than for the hydrogen-nitrogen or deuterium-nitrogen mixtures. The helium molecule, having the same mass as deuterium, is thus clearly shown to have a different field, being in fact harder than deuterium.

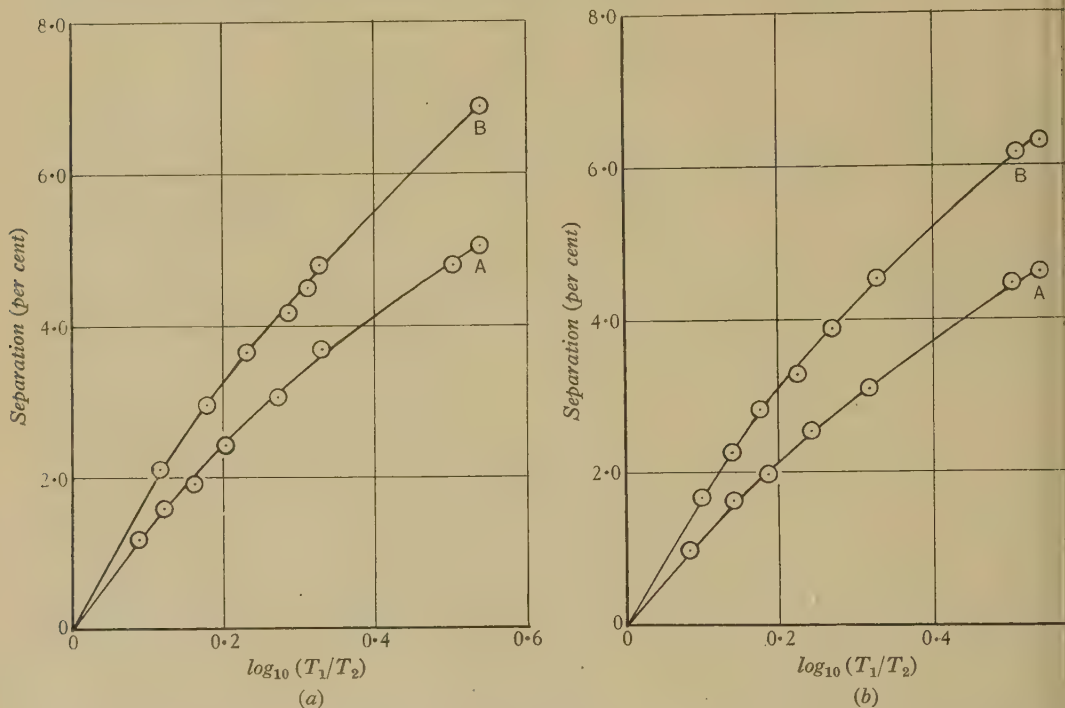


Figure 2. The variation of thermal separation with $\log(T_1/T_2)$ when $T_1 = 10^\circ \text{C.}$, $T_2 = 0^\circ \rightarrow -190^\circ \text{C.}$ (a) Hydrogen-nitrogen; A, 28.0 per cent and B, 42.7 per cent of hydrogen. (b) Deuterium-nitrogen; A, 28.1 per cent and B, 42.6 per cent of deuterium.

The third column of table 1 gives the values of the index q of the repulsive force, as found by interpolation in a series of corresponding values of R_t and q given by Chapman and Hainsworth⁽¹⁰⁾. These values apply to the special case when the mass and size ratios are very large, but the extension to the present case is unlikely to affect them greatly.

The variation of separation with temperature at low temperatures. The thermal separation occurring in mixtures of hydrogen-nitrogen and deuterium-nitrogen was measured as the cold-side temperature T_2 varied from room-temperature to -190°C. Two mixtures of deuterium-nitrogen were examined: one containing 42.6 per cent of deuterium and the other 28.1 per cent. These were compared with two hydrogen-nitrogen mixtures in which the proportion of hydrogen was the same as that of deuterium in the deuterium-nitrogen mixtures. The results are shown in figure 2.

It is seen that in deuterium-nitrogen mixtures, as in hydrogen-nitrogen mixtures, there is a departure at low temperatures from the linear relation between separation and $\log (T_1/T_2)$: that is, R_t is again a function of the temperature. In table 2 the

Table 2. Variation of R_t with temperature

Mixture	0° C.	-70° C.	-95° C.	-125° C.	-150° C.
H ₂ -N ₂	0.57	0.57	0.45	0.39	0.36
D ₂ -N ₂	0.58	0.58	0.45	0.38	0.34

values of R_t at different temperatures for the 42.6-per-cent-deuterium mixture are compared with those for the corresponding hydrogen mixture. The experimental values of k_t at different temperatures are obtained from the slope of the {separation, $\log (T_1/T_2)$ } curves and R_t is obtained as before from the ratio of the experimental and theoretical values of k_t .

There is no significant difference at any temperature between the values for the deuterium-nitrogen mixture and those for the hydrogen-nitrogen mixture.

§ 4. CONCLUSION

The results* show that the thermal separation ratio R_t is the same for deuterium-nitrogen mixtures as for hydrogen-nitrogen, both at normal temperatures and at low temperatures where R_t depends on the temperature. This means that, while the thermal separation in the deuterium mixtures is less than in the corresponding hydrogen mixtures, the difference is entirely accounted for by the difference in mass of the molecules. Consequently the fields of force of hydrogen and deuterium molecules appear to be similar. This is in agreement with the results obtained by Cleave and Maass⁽⁵⁾, who compared the viscosities of hydrogen and deuterium over a wide range of temperatures.

On the other hand, although the masses of the deuterium and helium molecules are the same, the thermal separation in helium-nitrogen mixtures is greater than in corresponding deuterium-nitrogen mixtures. The difference must here be attributed to a difference in the molecular fields.

§ 5. ACKNOWLEDGMENTS

We thank Prof. S. W. J. Smith for kindly providing facilities for this work in the Physics Department of the University of Birmingham; Dr T. L. Ibbs for advice and criticism; and Dr F. P. Bowden for a supply of deuterium oxide.

* An interesting paper by O. and G. Blüh⁽⁶⁾ has recently appeared in which are described thermal diffusion measurements made by means of an optical method. There is general agreement with similar measurements made by the katharometer method in this Department, except at low temperatures. There seems however to be an error in the method used by O. and G. Blüh for calculating the total separation from the observed change in concentration, and when this is corrected the low-temperature values agree well with those obtained⁽²⁾ by Ibbs and one of us (K. E. G.). This concordance of results obtained by entirely independent methods is gratifying.

REFERENCES

(1) THEORETICAL:

- (a) ENSKOG, D. *Phys. Z.* **12**, 538 (1911); *Ann. Phys.*, Lpz., **38**, 742 (1912).
- (b) CHAPMAN, S. *Proc. roy. Soc. A*, **93**, 1 (1916); *Philos. Trans. A*, **217** (1917).
- (c) CHAPMAN, S. and HAINSWORTH. *Phil. Mag.* **48**, 602 (1924).

Full references to other theoretical papers are given in (2).

- (2) IBBS, T. L., GREW, K. E. and HIRST, A. A. *Proc. phys. Soc.* **41**, 456 (1929).
IBBS, T. L. and GREW, K. E. *Proc. phys. Soc.* **43**, 142 (1931).
- (3) IBBS, T. L. and WAKEMAN, A. C. R. *Proc. roy. Soc. A*, **134**, 613 (1932).
- (4) IBBS, T. L. and UNDERWOOD, L. *Proc. phys. Soc.* **39**, 227 (1927).
- (5) VAN CLEAVE, A. B. and MAASS, O. *Canad. J. Res.* **12**, 1 (1935).
- (6) BLÜH, G. and O. *Z. Phys.* **90**, 12 (1934).

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THE ACCURATE DETERMINATION OF IONOSPHERIC EQUIVALENT HEIGHTS

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ABSTRACT. A method has been described for measuring the equivalent height of an ionized region of the upper atmosphere with an accuracy of ± 0.5 km. It has been shown that though the accuracy is of this magnitude the resolving-power of the apparatus, which is fixed by the width of the pulse used, is not so great, there being difficulties in determining the height difference of two pulses less than 5 km. apart. However, when certain precautions are taken it is possible to obtain height separations of the order of 5 km. with a fair degree of accuracy. With the aid of the apparatus described it has been shown that there are no sudden changes of height in either the E_1 or the F_2 region greater than those which might be expected from errors of measurement. The equivalent height of the so-called "abnormal E " region has been compared with that of E_1 and is shown to be not more than 3 or 4 km. greater. The frequency separation of the two critical frequencies for the ordinary and the extraordinary rays returned from the abnormal E region has been measured and is shown to be in agreement with the value to be expected on the magneto-ionic theory of the propagation of waves through an ionized medium. A discontinuity in the curve of height against frequency has been shown to exist at a frequency just less than 2 Mc./sec. This phenomenon, which was first noticed by Naismith at Slough two years ago, is shown to have all the characteristics of penetration and leads to the inference that there is a secondary maximum of ionization a few kilometres below the maximum of the E_1 region, somewhat similar to the ledge on the F region discovered by Appleton. For purposes of reference in the paper this maximum is called E_s . It has been shown that the height of the E_1 region is less in winter than in summer but that the diurnal variation of height shows a minimum of height several hours after midday. It is suggested that the winter minimum is due to a general increase in molecular density in the atmosphere caused by the lower temperatures of winter time.

§ 1. INTRODUCTION

EXPERIMENTAL investigations of the ionization of the upper atmosphere by means of wireless waves have resulted, after ten years of work, in the demonstration of the existence of two regions of ionization of sufficient density to produce reflection of waves of radio frequency. These are now known as the " E " and the " F " regions and close observation has established the presence of a subsidiary maximum of ionization on the lower side of the F region, which in England is apparent only in summer and in the daytime. There is also fairly detailed and accurate knowledge of the behaviour of this region in relation to variation of frequency of the propagated wave, time of day, time of year and, to a

E, F

certain extent, variation of latitude. The behaviour of the *E* region is not known with such accuracy, as the variations of equivalent height which it undergoes are much smaller than those of the upper *F* region.

In measurements of equivalent height by means of the frequency-change method of Appleton⁽¹⁾ or the echo method of Breit and Tuve⁽²⁾ the accuracy which is normally obtained is in the neighbourhood of ± 2 km. In the case of the frequency change method a change of 16 kc./sec. when the *E* region has an equivalent height of 100 km. produces 10 fringes representing P' , i.e. 200 km., the sender and receiver being near together. Thus to measure with an accuracy of ± 2 km. it is necessary to estimate one-fifth of a fringe, which is about the limit for a reliable estimate. In the case of the echo method with a cathode-ray oscillograph, the usual time base has a scale in which 10 mm. correspond to an equivalent height of about 50 km.; the diameter of the cathode-ray spot is more than 0.5 mm., so that the accuracy cannot be more than ± 0.5 mm., which represents ± 2.5 km., and is sometimes less. With the use of a Duddell oscillograph greater accuracy can be obtained, but large quantities of film are needed and the observations cannot be made at frequent intervals, so that the use of that instrument has not been very extensive.

The purpose of this research has been to investigate the behaviour of the *E* region in greater detail than has been usual, by increasing the accuracy of the measurement of the equivalent height.

§ 2. APPARATUS

It was decided that the simplest way of obtaining greater accuracy was to increase the length of the time base on a cathode-ray oscillograph, disposing successive short lengths of it one below the other, and to take frequent snap photographs of the echo pattern in order to obtain a faithful record of quick variations of equivalent height. A description of such a type of time base for use in television scanning⁽³⁾ gave a basis for construction, and in collaboration with Dr O. O. Pulley a suitable circuit was designed. The wiring diagram is given in figure 1. A 250-volt supply charges condenser C_1 through a variable resistance r_3 . When the voltage has risen to a critical value as set by the grid bias on the gas-filled relay T_1 , C_1 is discharged by the relay into condenser C_2 . Condenser C_2 has a much greater capacity than C_1 ,* so that C_1 is practically completely discharged. The second terminal of C_2 is earthed and the potential variations of the two condensers are amplified by single stages of resistance-capacity amplification and applied, that of C_1 to the *X* axis plates of the oscillograph and that of C_2 to one of the *Y* axis plates. The relay T_1 has its anode earthed through a similar relay T_2 while condenser C_2 is shunted by a power valve (A.C.P.). The grids of these last two components are connected in parallel through a resistance to a square form oscillation of fifty cycle frequency. Thus for half a cycle the grids are positive, the two condensers are virtually short circuited and the spot remains stationary on the

* The values are as follows: $C_1 = 0.05 \mu\text{F.}$, $C_2 = 2.0 \mu\text{F.}$

oscillograph screen. For the other half of the cycle the grids are negative and the long time scale is traced, forming a pattern as shown in figure 2 (a). By varying the resistance r_3 the charging rate of condenser C_1 can be varied, thus opening or closing the scale, while variations in the grid bias of the relay T_1 change the maximum voltage of C_1 and thus vary the length of each section of the time base. This is of great value when an echo happens to occur just at the end of a section, for a small change in the setting of the potentiometer r_4 will bring the echo properly on to that section and enable the equivalent height to be measured easily.

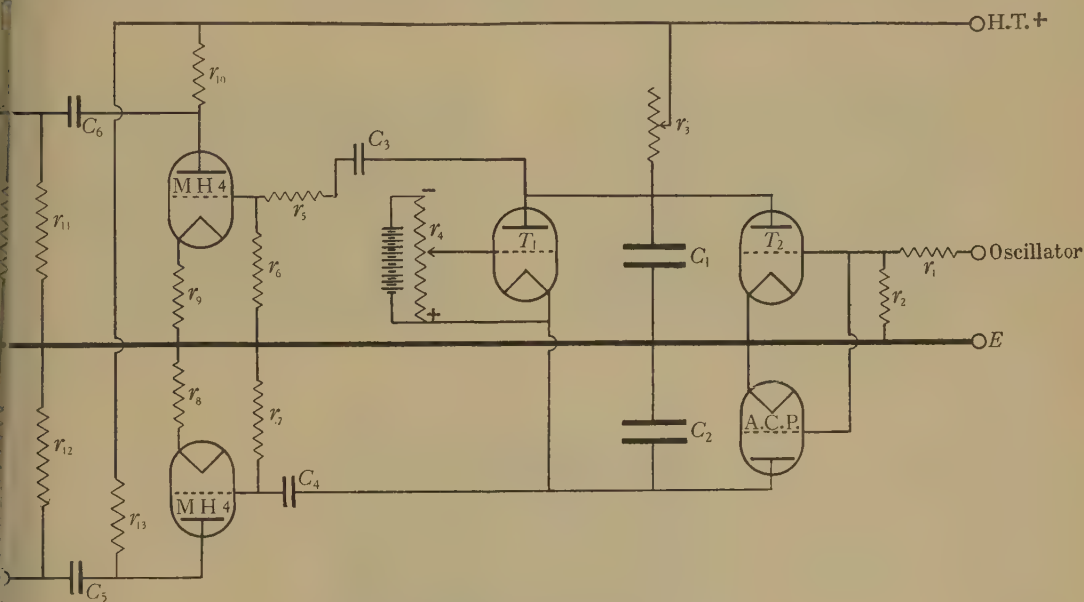


Figure 1. Circuit for open-scale time base.

The square-form oscillation was obtained from the oscillator in the time-base device usually used for the measurement of echo times. This oscillator could be locked in synchronism with the incoming pulse so that the ground-ray pulse was kept stationary at the beginning of the scale⁽⁴⁾. Usually the values of C_1 and r_3 were so arranged that 50 mm. on the time base represented 50 km. of equivalent height; thus measurement to the nearest millimetre gave an accuracy of ± 0.5 km.

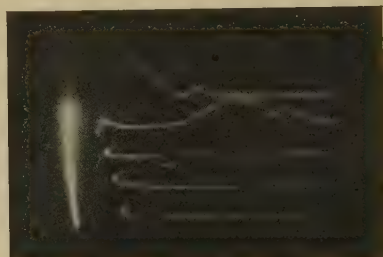
It will readily be realized that on such an open scale the pulse will be very broad, and as it is not possible to increase the gain of the receiving set proportionally, the rise of the front edge of the pulse will be slow and it will be difficult to make measurements accurately, if the foot of the pulse is taken as a reference point as is usual. It was just at the time when the apparatus was being constructed that O. O. Pulley, in a letter to *Nature*⁽⁵⁾, drew attention to the possibility of using the first differential of the voltage variation which forms the pulse to obtain the position of the peak of the pulse instead of the foot. A circuit such as he described was fitted by him to the receiving set, and figure 2 (c) shows the type of oscillographic record which was obtained. In figure 2 (a) is seen the time base with no signal

impressed; the small deflections mark off successive intervals of 50 km. In figure 2(b) is shown the effect of impressing a pulse in the normal way, to illustrate the difficulty of observing the beginning of the pulse accurately. In figure 2(c) the first differential of the pulse has been impressed. Here it is quite easy to fix the position of the peak of the pulse, for at that point the trace crosses the zero line at a definite angle instead of becoming asymptotic to it as in the previous case.

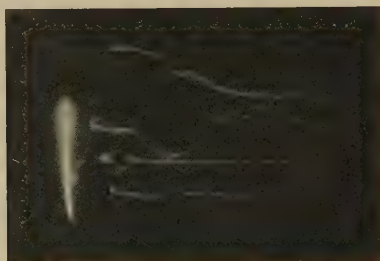
For recording purposes the trace in the tube was photographed with a film camera on standard cinematograph film so arranged that after each exposure of half a second the film was moved on through a distance equivalent to one frame by a ratchet device. This mechanism could be driven by a motor either at the rate



(a)



(b)



(c)

Figure 2.

of four exposures per minute or at the rate of one exposure every ninety seconds. If desired it could be operated by hand so as to take a photograph at any desired moment.

In order to measure the equivalent heights an auxiliary apparatus was constructed. This consisted of a brass frame in which the developed film could be slid under a square aperture of the same size as the frame aperture of the camera. Above this aperture was fixed a transparent positive of a photograph of standard millimetre graph paper taken with the film camera. A mirror directed light through both films, and the two were observed through a simple microscope with a magnification of about $3\times$. The positive formed a graticule of reference, the time marks on the trace gave intervals of 50 km., and by interpolation the equivalent height for each photograph could be determined quite quickly.

§ 3. OBSERVATIONS

The first use to be made of the apparatus was to search for sudden variations of equivalent height of both the *E* and the *F* regions, of a magnitude too small to be detected readily with apparatus of less accuracy. A number of runs on a constant frequency were taken for the *F* region, exposures being made every quarter of a minute. These runs showed a continuous variation of height with time, but there was no sign of any sudden change of height of the order of 4 km., what variation there was being of about the magnitude of the estimated experimental error. Observations at constant frequency on the *E* region gave slightly different results. The height generally remained constant, there being a slow change of a few kilometres in the space of 4 to 5 hours. While on some days the curve was practically a straight line with no variations greater than 1 km. due to experimental error, on other days there were quite large variations in an interval of 1 minute, some of the height-changes being as great as 10 km. Observations over a range of frequencies (generally called "a $P'-f$ run") showed that these changes occurred when the extraordinary component of the ray returning from the *E* region had an amplitude comparable with that of the ordinary component. When the extraordinary component was strongly absorbed, the height-variation was not greater than the magnitude of the experimental error, except for the slow change over a period of several hours.

A theoretical examination of the effect of the superposition of one pulse upon another with a very small time difference between them shows that the resultant is a single pulse as long as the two components are almost in phase, but that a change of amplitude or phase of either component produces a change in the position of the peak of the resultant. For example, where it is assumed that the pulse has the form $y = 1 + \cos \theta$ and the separation of the two components is one-tenth of a pulse-width, a change in amplitude of one of the components from zero to unity (i.e. to equality with the other component) will cause the peak of the resultant pulse to move one-twentieth of a pulse-width. In the case of a pulse whose width on the time scale is 50 km. this will mean a shift of 2.5 km. On the other hand if the two components should be out of phase and comparatively close together, the resultant is two pulses with a separation greater than the true separation of the components, one pulse being larger than the other unless the two components are equal in magnitude. Thus it happens that when the echo-amplitude of the extraordinary ray is smaller and exactly out of phase with the ordinary echo, a single peak is seen whose apparent equivalent height may be a tenth of a pulse-width greater or smaller than the true equivalent height. In general the situation is that while it is possible to obtain accuracy of determination of equivalent height with a value of ± 0.5 km. it is not possible to obtain a resolving power of anything like that figure, as this depends on the width of the pulse which in its turn is set by the frequency band-width which can be used in the receiving set.

In addition to observations on a steady frequency, occasional observations ($P'-f$ runs) were taken at noon over a range of frequency, the variation being

made in steps of about 0.05 Mc./sec., so that a graph of equivalent height against frequency could be plotted. These were for the purpose of investigating the *E* region only and so were not continued beyond that frequency at which the echo from the *E* region disappeared. During the period from June to November 1934 thirty-six such graphs were plotted and from them information has been gained

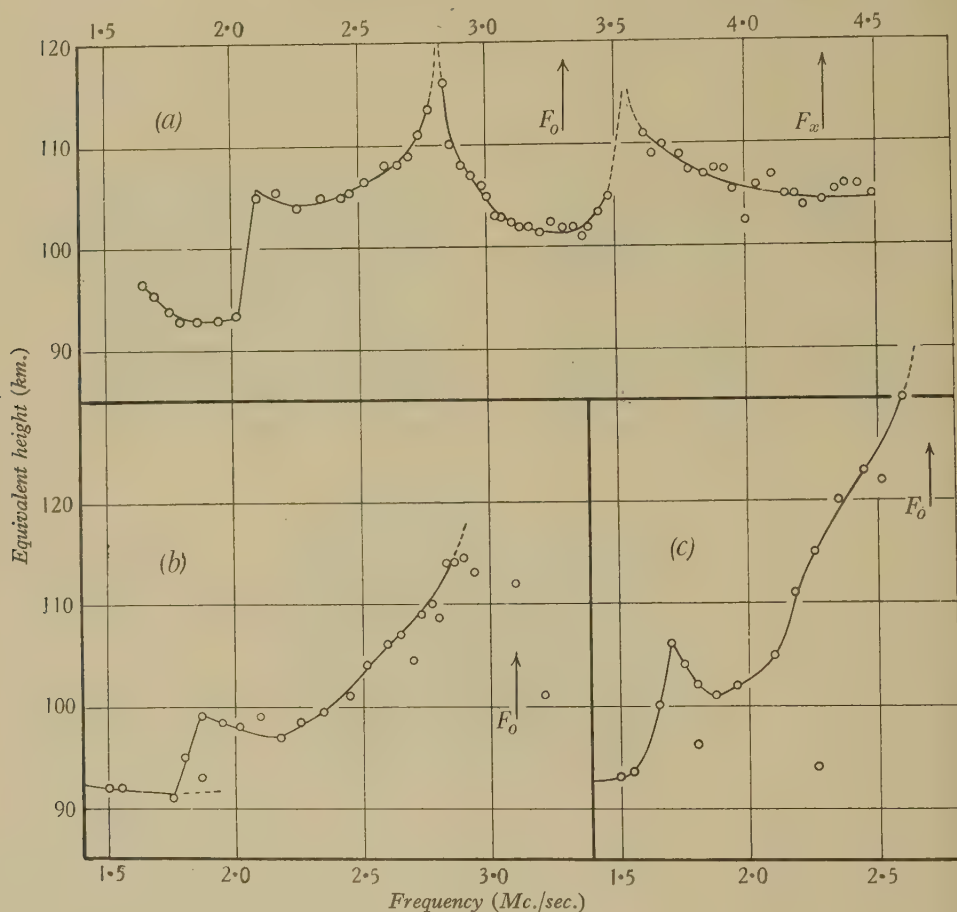


Figure 3. (a) August 28; (b) September 12; (c) October 12; Noon G.M.T.

under four heads. Three of the graphs have been reproduced in figure 3 as they illustrate most of the features to be discussed.

Usually, as the frequency is increased the equivalent height remains constant for a while, after which there is an increase accompanying the penetration of the region. Presently region *E* is penetrated and then reflection takes place from region *F*: see figures 3 (b) and 3 (c) where the appearance of the *F* echo is indicated by an arrow. On some days, especially in the summer, after penetration has taken place reflection continues from the *E* region, the equivalent height decreases, and for a time echoes

are observed from both regions; see figure 3 (a). This phenomenon has been called by E. V. Appleton "abnormal E "⁽⁶⁾ and must be due to some form of partial reflection caused by a very steep gradient of ionic density somewhere in the region. O. O. Pulley noticed in 1933 that this hump in the equivalent {height, frequency} curve sometimes repeated itself about 0.7 Mc./sec., and suggested that it was caused by the extraordinary component of the downcoming wave repeating the behaviour of the ordinary component. In the curves plotted with the open-scale time base this double hump has been observed quite often, and a table is given below showing the frequencies at which the equivalent height of the E region became a maximum and those at which the ordinary and the extraordinary components of the ray returning from the F region began to be received.

abnormal
 E

Table 1

Date	$f_{(\max,1)}$ (Mc./sec.)	$f_{(\max,2)}$ (Mc./sec.)	$f_{E_1}^0$ (Mc./sec.)	$f_{E_1}^x$ (Mc./sec.)	$f_{(\max,2)}-f_{(\max,1)}$ (Mc./sec.)	$f_{E_1}^x-f_{E_1}^0$ (Mc./sec.)
June 13	3.6	3.8	3.6	4.2	0.2	0.6
14	2.95	3.65	3.4	4.2	0.7	0.8
15	3.1	3.9	3.5	4.2	0.8	0.7
20	3.3	4.1	3.8	4.7	0.8	0.9
22	3.3	4.1	4.1	4.7	0.8	0.6
Aug. 14	3.0	3.9	3.3	4.2	0.9	0.9
15	2.9	3.6	3.2	4.2	0.7	1.0
20	2.9	3.8	3.2	3.8	0.9	0.6
24	3.1	3.7	3.4	4.6	0.6	1.2
27	3.0	3.5	3.4	4.3	0.5	0.9
28	2.8	3.7	3.3	4.3	0.9	1.0
Sept. 11	2.9	3.5	3.1	4.2	0.6	1.1
15	2.7	3.5	3.0	No data	0.8	—
Oct. 19	2.8	3.3	2.9	No data	0.5	—
Mean values					0.69	0.86

In the columns from the second to the fifth are given in order the frequencies at which E reached its first and second maximum heights and at which the ordinary and extraordinary components of F began to appear. These second two frequencies have been taken as the critical frequencies for the E region and have been labelled as such; the first two frequencies are simply called $f_{(\max,1)}$ and $f_{(\max,2)}$. In every case except one in this table it will be seen that the ordinary ray began to be returned from the F region after the first maximum height in the E region has been observed but before the second maximum height had occurred. Thus although it was not possible to obtain the state of polarization of the E echo at various parts of the curve, there is little doubt that the first maximum corresponds to penetration of the E region by the ordinary ray while the second maximum is due to penetration by the extraordinary ray. As further evidence the figures in the sixth column may be taken. These are the differences between the two frequencies for maximum height, and their mean value is 0.69 Mc./sec., a figure which is quite in agreement with the frequency separation to be deduced from the magneto-ionic theory of wave-propagation.

$f_{(\max,1)}$,
 $f_{(\max,2)}$

After penetration of the E region has taken place the decreasing equivalent height of the abnormal E region can be explained in terms of the decreasing retardation in E region. As the frequency is increased above that for which the μ is nearly zero and the group velocity is very small, the retardation gradually decreases and the equivalent height returns to normal. Now however it must be assumed that the point in the region at which reflection is taking place is not necessarily the lower boundary of the E region, but may be some very steep ionization gradient which produces a partial reflection of the wave, since the F -region echo is simultaneously observed.

In order to get some idea of the position of this sudden change of ionic density the equivalent heights were measured on the curves, first at low frequencies where it seemed probable that the equivalent height represented almost the lower boundary of the region, being unaffected either by penetration of the layer or by group retardation of the wave, and secondly at the highest frequencies, where the curve had once again become flat, the reflection being partial now and the group retardation negligible. It was not possible to do this for all the curves where abnormal E was present, for sometimes the echoes faded out before the curve became sensibly flat again, so only part of the thirty-six curves is represented in table 2.

Table 2

Date	Equivalent height of E_1 region (km.)	Equivalent height of abnormal E (km.)	Height of abnormal E less height of E_1 (km.)
June 13	102	102	0
14	108	103.5	-4.5
22	104	110	6
July 2	103	106	3
16	98	101	3
17	99	108	9
Aug. 15	99	100	1.5
27	102	107	5
28	105	105	0
Sept. 6	94	95	1
18	95	103	8
Oct. 18	91	90	-1
19	100	100	0
19*	95	95	0
29†	95	95	0
Nov. 21	92	92	0
Mean values	98.87	100.78	1.9

* 11.0 G.M.T.

† 13.0 G.M.T.

This table shows that except in two cases the abnormal E region is at the same height as the normal E or a few kilometres higher. If it is true that the echo is due to some form of partial reflection at a surface of discontinuity, then the height measured will be a true height except for such group retardation as may remain in consequence of the final frequency of reflection not being sufficiently above the critical frequency for E . On the other hand the height measured for normal E is an equivalent height and therefore somewhat greater than the true height of the

region. The result is to indicate that the abnormal E region is always at a greater height than the lower boundary of the E region and therefore cannot be identified with an increase of the ionization-gradient at the lower boundary. It is apparently a steep gradient within the layer itself.

One new phenomenon which has been demonstrated by these $\{P', f\}$ curves is the presence of a discontinuity in equivalent height at a frequency lower than the critical frequency for the ordinary ray returned from the E region. This is shown quite clearly in the curves of figure 3 together with the fact that the discontinuity is accompanied by group retardation and presents all the characteristics of penetration of an ionized region. In addition there is evidence in two of the curves, and in others not shown, that, after the discontinuity, reflections from the smaller equivalent height, which may be due to an extraordinary ray, are recorded. At the time when this phenomenon was being further investigated, information was received from Mr Naismith at the Radio Research Station, Slough, that since early in 1933 a peculiarity had been observed in the $\{P', f\}$ curves at frequencies round about 2 Mc./sec. This took the form of an apparent group-retardation phenomenon, but the accuracy of the apparatus was not sufficient to determine if there was really any change of height or not. During a visit to Slough the curves taken at the Halley Stewart Laboratory were compared with those taken at Slough and it seemed quite definite that the phenomena being observed at the two places were the same, the frequencies being in agreement with one another. In addition the Slough curves showed a repetition of the phenomenon at a frequency about 0.7 Mc./sec. higher than the first. This bears out the suggestion that the first discontinuity is due to penetration by an ordinary component of the returning ray while the second corresponds to penetration by the extraordinary component. At the Halley Stewart Laboratory, where the noise-level is higher than at Slough, though it is possible to observe the ordinary component the extraordinary component is generally too weak through absorption to give a visible echo except at values of set-gain made impossible by noise. Some of the information bearing on this suggestion is summarized in table 3. In the columns from the second to the fourth are shown the critical frequency for this suggested region, which must be similar in nature to the F_1 shelf below the F_2 region, and will be provisionally referred to as E_s ; the critical frequency for the ordinary ray returned from the E_1 region; and the difference between these two frequencies. In the last three columns are given the mean equivalent height for frequencies between 1.5 Mc./sec. and the critical frequency for the E_s region, the mean height for frequencies between that and 2.3 Mc./sec. and the difference between these two heights. These figures show that the critical frequency for this region bears a fairly constant relation to that for the E region, being about 0.9 Mc./sec. below it, while the equivalent height is about 5 km. lower than that of the E region.

E_s

A previous argument applies to a certain extent here, for while the equivalent height of the E_s region is probably not accompanied by group retardation, there is a possibility that the height of the E region is increased owing to group retardation in the E_s region. Thus the difference of height may very well be too large, and one

would regard 2-3 km. as about the right figure. This makes the heights of normal E_1 , abnormal E , and E_s all lie within a range of 6 or 7 km. of equivalent height and agrees with previous observations on the E region that variations of ionic density take place over much smaller height-ranges in the E region than in the F region. One cannot help associating this with the results of many theoretical considerations, to the effect that variations of pressure with height are greater at 100 km. than at 200 km.

In figure 4 the equivalent-height data of table 3 have been plotted to bring out the nature of another phenomenon, the variation of equivalent height with time of year. This figure shows that the heights of both the E_1 and the E_s regions were greatest in the summer and became less as the winter advanced. This is a variation

Table 3

Date	f_{E_s} (Mc./sec.)	$f_{E_1}^0$ (Mc./sec.)	$f_{E_1}^0 - f_{E_s}$ (Mc./sec.)	Mean height 1.5 Mc./sec. to f_{E_s} (km.)	Mean height f_{E_s} to 2.3 Mc./sec. (km.)	Increase of height (km.)
July 17	1.7	2.8	1.1	97	99	2
Aug. 20	1.85	2.9	1.05	99	102	3
24	1.9	3.1	1.2	99	102	3
27	2.05	3.0	0.95	97	102	5
28	2.05	2.8	0.75	95	105	10
29	2.25	3.0	0.75	98	106	8
Sept. 10	1.9	3.1	1.2	90	95	5
12	1.9	2.9	1.0	92	98	6
15	1.7	2.7	1.0	98	102	4
18	1.8	2.85	1.05	93	95	2
Oct. 12	1.7	2.6	0.9	95	101	6
17	1.7	2.65	0.95	93	102	9
19	1.8	2.8	1.0	95	100	5
19	1.9	2.65	0.75	94	95	1
23	1.7	2.5	0.8	90	97	7
Nov. 6	1.9	2.7	0.8	95	97	2
8	1.7	2.45	0.75	93	106	13
Mean values			0.93			5.3

in a sense opposite to that experienced by the F_2 region and requires some amendment of current theory for its explanation. Chapman has given an explanation of the well-known shape of the {ion-density, height} curve as due to the fact that the intensity of the ionizing agent (ultraviolet light) increases with altitude while the pressure of the air (molecular density) decreases with height⁽⁷⁾. Various theoretical estimates of the pressure-variation with height indicate that up to 100 km. (the height of the E region) the decrease in pressure per kilometre rise is large, while above 100 km. this rate of decrease is much smaller⁽⁸⁾. At the place where the pressure begins to rise comparatively steeply with decrease of height a sudden stop will be put to the effectiveness of free electrons in affecting the refractive index for radio-frequency waves by a quick decrease in their mean free paths. Thus the lower boundary of the E_1 region will coincide very nearly with the position of this

bend in the {pressure, height graph}. A drop in temperature of the atmosphere as a whole will move the position of this bend towards the earth and produce a decrease in the equivalent height of the E_1 region. It might be expected that if this is the case for variations of temperature throughout the year it would also be true for variations during the course of a day. A number of continuous observations of equivalent height have been carried out with rays of constant frequency from sunrise to sunset on certain days in order to investigate this possibility. It was necessary of course to make sure that the height observed was the true equivalent height and was not increased at any time by penetration or group retardation, and for this purpose the steady frequency was made as low as possible and on several occasions during the day $P'-f$ runs were made in order to ascertain if the equivalent {height, frequency} curve was flat at the frequency in use. In the curves the penetration associated with the appearance of the echo at sunrise and its

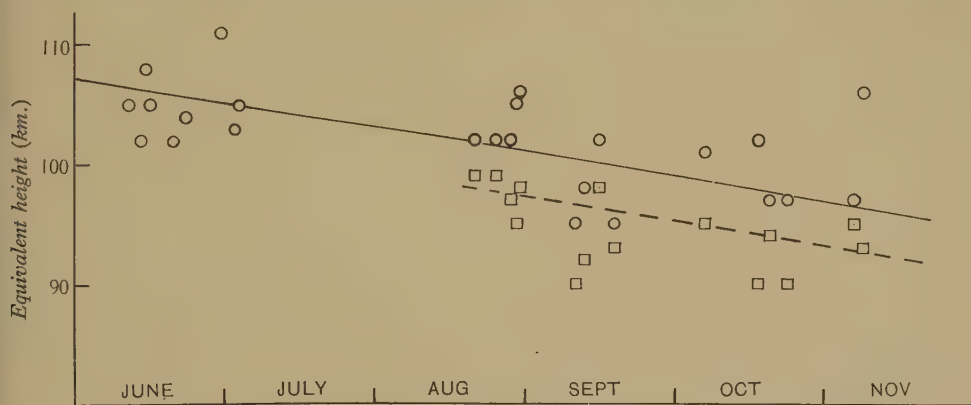


Figure 4. Equivalent height of the ionosphere. \circ , region E; \square , region E_s .

disappearance at sunset can be seen, but during the intermediate hours, when the true equivalent height of the region was being measured there was a decrease of height towards the middle of the day followed by an increase towards sunset. The position of the minimum of height was not always at midday but was sometimes $1\frac{1}{2}$ –3 hours later. This result is not entirely contradictory of the suggestions advanced above, for the variations in temperature of the whole of the atmosphere above a given point on the earth are not likely to immediately follow the altitude-changes of the sun but will have an appreciable lag. This lag may be so large a fraction of the 24-hour period of the earth's rotation that the pressure-variation may be almost in opposition to the intensity variation of the ultraviolet light, so as to flatten out the {equivalent-height, time} curve, or else to distort it. The latter process seems to be the case in the curves where the time of minimum height is later than midday. On the other hand, the very slow change of mean day temperature from summer to winter will be faithfully followed by the whole of the atmosphere and so give a minimum of equivalent height in winter.

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REFERENCES

- (1) APPLETON, E. V. and BARNETT, M. A. F. *Proc. roy. Soc. A*, **109**, 621 (1925).
- (2) BREIT and TUVE. *Terr. Magn. atmos. Elect.* **30**, 15 (1925) and *Nature*, Lond., **116**, 357 (1925).
- (3) BEDFORD and PUCKLE. *J. Instn elect. Engrs*, **75**, 63 (1934).
- (4) PULLEY, O. O. *Proc. phys. Soc.* **46**, 853 (1934).
- (5) ——— *Nature*, Lond., **133**, 576 (1934).
- (6) APPLETON and NAISMITH. *Proc. roy. Soc. A*, **150**, 690 (1935).
- (7) CHAPMAN. *Proc. phys. Soc.* **43**, 26 and 484 (1931).
- (8) PEDERSEN. *Propagation of Radio Waves*, pp. 39-44.

ON THE DEVELOPMENT OF THE QUANTUM EQUATION AND A POSSIBLE LIMIT TO ITS APPLICATION

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ABSTRACT. The first-order equation of the quantum theory is developed by applying a parallel displacement to the matrix length of a vector. The quantum theory reveals itself as a law of parallel displacement from which a modification of Weyl's theory is deduced. In this modification a term containing the mass of a charged particle occurs as well as terms containing the charge and electromagnetic potential. The principle of minimum proper time emerges from this result as a limitation of the application of the quantum equation to a particle in an electromagnetic field.

§ 1. INTRODUCTION

THE suggestion that the quantum theory may be regarded as a manifestation of a particular form of natural metric was made some time ago⁽¹⁾. It was shown that Schroedinger's equation could be regarded as a condition satisfied by a particular metrical function described as a scale factor and that it led directly to a modification of Weyl's theory. In the latter the measured lengths of physics are subject to changes upon undergoing parallel displacements, the magnitudes of the changes being dependent on the path of displacement. According to Weyl the changes of length are related to the components of electromagnetic potential and the non-integrability of the change corresponds to the same property of this potential. But if the theory in this form be applied directly to the space and time of physics, it leads to a curious result. One would conclude that atoms must emit spectral lines of a frequency dependent upon the potential of the field in which they are situated. In the course of time, since atoms occupy very different fields, there would be no lines of a definite frequency from differently placed atoms. In discussing this fact Weyl took the point of view that his parallel displacement was of the nature of an ideal process and that his metrical field could not be directly defined as a result of measurements with instruments. If we have to take this view with regard to it, the theory seems to be robbed of physical content.

But the theory of parallel displacement, when we modify it by recognizing it as manifested in the quantum theory, recovers its physical content, for it makes the change of length periodic with the path of displacement. The quantum paths of the theory of Bohr and Sommerfeld are those for which the change goes through a

complete number of periods and the displaced vector recovers its original length. The shortest length over which such a recovery is possible is h/m_0c when a particle of rest mass m_0 is occupying the path of the displacement. By a different procedure London⁽²⁾ reached the same conclusion in a contribution to the subject which was especially designed to remove the artificial element inherent in Weyl's explanation of his point of view.

Since these suggestions were first made, the quantum theory has developed considerably and the first-order equation has been introduced by Dirac together with matrices of a fundamental character not unlike that possessed by axes of coordinates. In spite of the radical change in the form of the theory which results, the conviction that the branch of physics here concerned is a metrical manifestation has grown and has been gradually given a more satisfactory form of expression than was previously possible. It has become evident that the fundamental equation of the theory is of the nature of a law of parallel displacement. The development of the equation from a simple geometrical idea becomes possible, the idea requiring for its expression the concept of a matrix length.

In a recent contribution⁽³⁾ to this question a somewhat general development has been given, that it appears that a simpler theory is possible and that it leads to unification of the microscopic and macroscopic domains of physics.

It is our present purpose to give an account of this theory.

§ 2. MATRIX LENGTH AND PARALLEL DISPLACEMENT

We make the supposition that the measured length of a vector having a typical component A_m is represented in the theory by l where

$$l = \alpha^m A_m \quad \dots\dots(1),$$

α^m, m α^m denotes a typical fundamental matrix, and m may have the values 1-4. A set of four such matrices is associated with each point and they are to be regarded as possessing the character of vectors and to be functions of the coordinates.

This length may be regarded as a fundamental element of microscopic physics or of matrix geometry. Mimura⁽⁴⁾ who has also introduced this idea speaks of the geometry as "wave geometry". An important link between this geometry and what we may describe as macroscopic geometry is a relation due, in the first place, to Tetrode. This relation will be expressed in the form

$$\alpha^m \alpha^n = g^{mn} I + s^{mn} \quad \dots\dots(2).$$

I, s^{mn} I is the unit matrix and s^{mn} is the antisymmetric part of the product $\alpha^m \alpha^n$. It corresponds to the spin matrix of the quantum theory. The components g^{mn} are the gravitational components of the theory of relativity and thus we have in equation (2) a link between the quantum theory and the theory of relativity or, as we may say, between microscopic and macroscopic physics. When a vector A_m undergoes a parallel displacement, it is understood that its components change by an amount dA_m given by

$$dA_m = \Delta_{mn}{}^l A_l dx^n \quad \dots\dots(3).$$

Δ_{mn}^l is undetermined, but we shall interpret it by means of the equation

$$\Delta_{mn}^l = \Gamma_{mn}^l + T_{mn}^l \quad \dots\dots(4),$$

where Γ_{mn}^l is the Christoffel bracket expression and T_{mn}^l will be restricted in accordance with the requirements of the physical theory. This means that certain limitations will be placed upon it by the quantum theory and by the theory of electromagnetism.

From equation (1)

$$\begin{aligned} dl &= \left(\frac{\partial \alpha^p}{\partial x^m} + \Delta_{nm}^p \alpha^n \right) A_p dx^m \\ &= K_m^p A_p dx^m, \end{aligned} \quad \dots\dots(5)$$

where the matrix K_m^p denotes the expression in the bracket.

§ 3. THE INVARIANT LENGTH

In accordance with an earlier suggestion made in connexion with Weyl's theory of electromagnetism, we shall suppose that each point of space is provided with a scale factor. This is a function of the coordinates and in the present case it is a matrix ψ , which we suppose to consist of a single column of values ψ_{1n} , where n can have the values 1 to 4, the other components of the matrix being zero. It is convenient to denote the components ψ_{1n} by ψ_n for simplicity.

This matrix combined with the matrix l produces a matrix of invariant length L , thus

$$L = l\psi.$$

The invariance refers to a parallel displacement, so that

$$\begin{aligned} dL &= 0, \\ d(l\psi) &= dl\psi + l d\psi = 0. \end{aligned}$$

From equation (5)
$$\left(\alpha^p \frac{\partial \psi}{\partial x^m} + K_m^p \psi \right) A_p dx^m = 0.$$

If this relation is to be true for all vectors and for all displacements, it follows that

$$\alpha^p \frac{\partial \psi}{\partial x^m} + K_m^p \psi = 0 \quad \dots\dots(6).$$

This equation is in the form of a mixed tensor and if we write $p = m$ and sum over all values of m , we obtain through the process of degeneration of a tensor

$$\alpha^m \frac{\partial \psi}{\partial x^m} + K_m^m \psi = 0 \quad \dots\dots(7).$$

But although this equation follows from equation (6), the converse is not true.

§ 4. COMPARISON WITH THE QUANTUM EQUATION

This equation is of the same form as Dirac's equation which forms the basis of the quantum theory and is the only means we have of approaching the problems of atomic physics. The development of equation (7) from a simple geometrical and metrical idea reveals the quantum equation as the manifestation of this concept

in the world of physics. We expect to obtain from physics some information about the form of K_m^p . Actually a comparison with the quantum equation gives us the form of K_m^m , the degenerated form of K_m^p .

Dirac's equation is

$$\alpha^m \frac{\partial \psi}{\partial x^m} - \frac{2\pi i e}{hc} \phi_m \alpha^m \psi + \frac{2\pi i m_0 c}{h} \alpha_0 \psi = 0 \quad \dots\dots(8).$$

e This equation is applied to a particle of rest mass m_0 , carrying a charge e , in an
 ϕ_m electromagnetic field with potential components ϕ_m and, if we make use of equation (2), we can add "in a gravitational field".

α_0 The matrix α_0 is additional to the matrices α^m , and in Dirac's theory it must satisfy the relations

$$\left. \begin{aligned} \alpha^m \alpha_0 + \alpha_0 \alpha^m &= 0 \\ \alpha_0^2 &= I \end{aligned} \right\} \quad \dots\dots(9).$$

These five matrices are essential in the theory and they must be linearly independent.

We adopt the relations (9) together with (2). The equations (7) and (8) become identical if K_m^m be chosen as follows:

$$K_m^m = -\frac{2\pi i e}{hc} \phi_m \alpha^m + \frac{2\pi i m_0 c}{h} \alpha_0 \quad \dots\dots(10).$$

This means that at any point of space the law of parallel displacement, as it is expressed by equation (7), is determined by ϕ_m , the mass m_0 and an additional matrix α_0 .

From equations (4), (5) and (10) we deduce

$$\frac{\partial \alpha^m}{\partial x^m} + \Gamma_{nm}^m \alpha^n + T_{nm}^m \alpha_n = -\frac{2\pi i e}{hc} \phi_m \alpha^m + \frac{2\pi i m_0 c}{h} \alpha_0 \quad \dots\dots(11).$$

When both gravitational and electromagnetic fields are absent, the term in $m_0 c$ in equation (8) still persists. In this case the α^m are constants and the Γ_{nm}^m and ϕ_m vanish so that

$$T_{nm}^m \alpha^n = \frac{2\pi i m_0 c}{h} \alpha_0 \quad \dots\dots(12).$$

§ 5. RECONSIDERATION OF THE FORMULA FOR CHANGE OF LENGTH

This introduces a difficulty for it means that α_0 is not linearly independent of the α^n . It is true that the T_{nm}^m may contain an arbitrary function which will introduce the necessary element of freedom in another way. But this procedure leads to complications and it seems desirable to remove the difficulty by other means. We must introduce α_0 into equation (7) independently of the T_{nm}^m . There is an obvious way of doing this by means of the α^m . These matrices are like axes of coordinates and it is reasonable to suppose that in using them as reference matrices at different points we must have some particular method in relating them as we pass from one

point to another. It is somewhat as if we had a parallel displacement of the matrices. Thus we might adopt the following expression for the change of α^m as a result of a parallel displacement:

$$\Delta\alpha^m = -\delta_n^m a \alpha_0 \Delta x^n \quad \dots\dots(13).$$

We use this form of expression since it is our intention to make it as simple as possible, in accordance with our requirements in the quantum theory. Thus δ_n^m will have the value 1 when $m=n$, otherwise it is zero. Clearly a more general theory is possible with $\delta_n^m \alpha_0$ as a more general matrix Λ_n^m . a is a constant which we shall fix later.

We can say that the matrices (α^m) are equal at two points when they have the values (α^m) and ($\alpha^m + \Delta\alpha^m$) at these points respectively. Thus in passing from one point to the other α^m undergoes the change $\partial\alpha^m/\partial x^n$ on account of the change of coordinates, and since $\Delta\alpha^m$ is the change required when the matrix sets are regarded as equal, the total change in passing between the two points is

$$\left(\frac{\partial\alpha^m}{\partial x^n} \Delta x^n - \Delta\alpha^m\right), \text{ equal to } \left(\frac{\partial\alpha^m}{\partial x^n} + \delta_n^m a \alpha_0\right) \Delta x^n.$$

This procedure suggests that there is some additional variation in the α^m in passing along the line between the two points which is not accounted for by simply considering the four coordinates (x^m). We shall return to this point later after applying this new variation to the change of length.

Returning now to equation (5) and taking account of this new element of variation, we obtain instead of that equation

$$\begin{aligned} dl &= \left(\frac{\partial\alpha^p}{\partial x^m} + \delta_m^p a \alpha_0 + \Delta_{nm}^p \alpha^n\right) A_p dx^m \quad \dots\dots(14) \\ &= K_m^p A_p dx^m, \end{aligned}$$

where K_m^p has now the value given by

$$K_m^p = \frac{\partial\alpha^p}{\partial x^m} + \delta_m^p a \alpha_0 + \Delta_{nm}^p \alpha^n \quad \dots\dots(15).$$

Thus by equation (8) although K_m^p retains the same value, when we pass to the quantum equation, the term in α_0 is no longer associated with T_{nm} . We have now

$$\frac{\partial\alpha^m}{\partial x^m} + \Delta_{nm}^m \alpha^n = -\frac{2\pi ie}{hc} \phi_m \alpha^m \quad \dots\dots(16)$$

instead of equation (11).

The matrix α_0 has an independent place in the theory, being concerned with matrix displacement. The quantum equation requires

$$\delta_m^m a \alpha_0 = \frac{2\pi i m_0 c}{h} \alpha_0 \quad \dots\dots(17),$$

and since summation is implied,

$$4a = \frac{2\pi i m_0 c}{h} \quad \dots\dots(18).$$

§ 6. AN IMPORTANT RELATION

From equation (2) we obtain Tetrote's relation

$$2g^{mn} = \alpha^m \alpha^n + \alpha^n \alpha^m,$$

whence
$$2 \frac{\partial g^{mn}}{\partial x^i} = \frac{\partial \alpha^m}{\partial x^i} \alpha^n + \alpha^m \frac{\partial \alpha^n}{\partial x^i} + \frac{\partial \alpha^n}{\partial x^i} \alpha^m + \alpha^n \frac{\partial \alpha^m}{\partial x^i}$$

$$= (K_l^m - \delta_l^m a \alpha_0 - \Delta_{rl}^m \alpha^r) \alpha^n + \text{etc.}$$

by equation (15).

If we remember the relation (4) and the identity satisfied by the gravitational components g^{mn} together with equation (9), we obtain

$$2 (g^{rn} T_{rl}^m + g^{rm} T_{rl}^n) = (K_l^m \alpha^n + \alpha^n K_l^m) + (K_l^n \alpha^m + \alpha^m K_l^n) \dots (19).$$

This determines the part of $g^{rn} T_{rl}^m$, which is symmetrical in m and n , in terms of the parallel displacement matrix K_l^m .

§ 7. CHANGE OF LENGTH IN MACROSCOPIC SPACE DURING A PARALLEL DISPLACEMENT. MODIFICATION OF WEYL'S THEORY

The square of the length of a vector with components A_m is determined in the theory of relativity by

$$l^2 = g^{mn} A_m A_n \dots (20).$$

On account of Tetrote's relation this can be regarded as the square of the matrix length, since

$$l^2 = \alpha^m A_m \alpha^n A_n = g^{mn} A_m A_n,$$

the antisymmetric part of $\alpha^m \alpha^n$ dropping out in this case. In a parallel displacement of the vector A_m , we obtain a change of length given by

$$\delta l^2 = \left(\frac{\partial g^{mn}}{\partial x^i} + \Delta_{rl}^m g^{rn} + \Delta_{rl}^n g^{rm} \right) A_m A_n \delta x^i$$

$$= (g^{rn} T_{rl}^m + g^{rm} T_{rl}^n) A_m A_n \delta x^i \dots (21).$$

Thus it is the symmetrical part of $g^{rn} T_{rl}^m$ in m, n which determines the change in length, and by equation (19) this is determined by the matrix K_l^m .

Weyl's theory of electromagnetism consists in assigning a value to the expression ϕ_l in brackets in equation (21). He chose, in fact, the value $2g^{mr} \phi_l$ so that in his theory

$$\frac{\delta l^2}{l^2} = 2\phi_l \delta x^l$$

or

$$\frac{\delta l}{l} = \phi_l \delta x^l \dots (22).$$

In this equation l denotes the scalar length and is not, of course, a matrix.

It seems clear from equation (10) that in the present theory ϕ_l will be associated with the factor $2\pi i e / hc$, since the expression (19) relates T_{rl}^m with the matrix K_l^m .

We thus identify the symmetrical part of $g^{rn} T_{rl}^m$ with $-(2\pi i e / hc) g^{mn} \phi_l$.

According to equation (19) this requires that

$$(K_l^m \alpha^n + \alpha^n K_l^m) + (K_l^n \alpha^m + \alpha^m K_l^n) = -\frac{8\pi i e}{hc} g^{mn} \phi_l \dots (23).$$

This means that the symmetrical part of $(K_l^m \alpha^n + \alpha^n K_l^m)$ is equal to

$$-(4\pi ie/hc) g^{mn} \phi_l.$$

If we write $l=m$ and sum over the values of m , we obtain as part of

$$(K_m^m \alpha^n + \alpha^n K_m^m)$$

the expression $-(4\pi ie/hc) \phi^n$, showing how ϕ^n is introduced into the theory through K_m^m as required by equation (10).

The discussion has been concerned with the symmetrical parts of certain quantities entering the equations and we have omitted any reference to the anti-symmetrical parts. These have not been determined by comparison with the quantum theory but we must examine whether any special conditions are required by the theory which in any way limit them.

§ 8. THE ANTISYMMETRIC PART OF T_{mn}^l

Let us suppose that the quantity T_{mn}^l introduced in equation (4) consists of a part S_{mn}^l symmetric in m, n and of A_{mn}^l antisymmetric in these suffixes. The theory requires us to relate T_{mn}^l with the electromagnetic potential in accordance with equations (19) and (23) and the relation enables us to modify Weyl's theory in accordance with equation (21). The circumstances are similar to those existing in Eddington's generalization of the theory of parallelism.

If we make use of a relation introduced by him⁽⁵⁾, the application of our theory can be easily understood although it may not be necessary to limit ourselves to the particular form employed. In the theory Γ_{mn}^l is taken to be symmetric in m, n and thus differs from our case. Let us write

$$S_{mn}^l = a' (g_{mn} \phi^l - \delta_m^l \phi_n - \delta_n^l \phi_m),$$

where a' is a constant and is equal to $\pi ie/hc$ in the present application. If we form the expression $g^{rn} T_{rl}^m$, we now obtain

$$g^{rn} T_{rl}^m = a' (\delta_l^n \phi^m - \delta_l^m \phi^n - g^{nm} \phi_l) + g^{rn} A_{rl}^m \dots\dots(24).$$

The part of this symmetrical in m, n is

$$\frac{1}{2} (g^{rn} T_{rl}^m + g^{rm} T_{rl}^n), \text{ equal to } -a' g^{nm} \phi_l + \frac{1}{2} (g^{rn} A_{rl}^m + g^{rm} A_{rl}^n) \dots(25).$$

According to equation (23) this expression is equal to $-(2\pi ie/hc) g^{mn} \phi_l$ and thus with the above value of S_{mn}^l we have to satisfy the further condition

$$g^{rn} A_{rl}^m + g^{rm} A_{rl}^n = -\frac{2\pi ie}{hc} g^{mn} \phi_l \dots\dots(26).$$

Let us turn to the effect of this upon equation (16), which contains

$$\Delta_{nm}^m = \Gamma_{nm}^m + T_{nm}^m = \Gamma_{nm}^m + S_{nm}^m + A_{nm}^m.$$

The value of S_{nm}^m is $-(4\pi ie/hc) \phi_m$, as may be seen from the above value of S_{mn}^l . In order to obtain A_{nm}^m , multiply equation (26) by g_{pn} and write $m=l$, summing over the values of m .

We obtain

$$A_{pn}^m = -\frac{2\pi ie}{hc} \phi_p.$$

Thus equation (16) becomes

$$\frac{\partial \alpha^m}{\partial x^m} + \Gamma_{nm}^m \alpha^n = \frac{4\pi ie}{hc} \phi_n \alpha^n \quad \dots\dots(27).$$

It is interesting to note that equation (19) is satisfied if K_l^m contains an expression of the form $(\alpha^m \Gamma_l - \Gamma_l \alpha^m)$, where Γ_l is a matrix. The use of equation (15), in deriving equation (19) from which $(\frac{\partial a^p}{\partial x^m} + \Gamma_{nm}^p \alpha^n)$ has vanished, thus suggests that this expression is of the above form and that we can write

$$\frac{\partial \alpha^p}{\partial x^m} + \Gamma_{nm}^p \alpha^n = \alpha^m \Gamma_l - \Gamma_l \alpha^m \quad \dots\dots(28).$$

This particular relation is of great importance in Schroedinger's theory⁽⁶⁾ of the generalized quantum equation.

§ 9. THE QUANTUM EQUATION AND THE ELECTROMAGNETIC THEORY

It is thus shown to be possible to develop a modification of the theory of electromagnetism proposed by Weyl as a consequence of the development of the quantum equation from the concept of the matrix length.

This indicates the existence of a close relation between the two branches of physics and provides us with a unitary theory embracing them. The theory includes also the relativity theory of gravitation, since the processes are those of general relativity. The modification of Weyl's theory coincides with that previously suggested and with that developed by London.

According to equation (20), l being used again as the scalar length,

$$\frac{\delta l}{l} = -\frac{2\pi ie}{hc} \phi_m \delta x^m,$$

corresponding to a scale factor $\exp \{(2\pi ie/hc) \int \phi_m dx^m\}$, for clearly this factor, multiplied by l , gives an invariant length.

F This suggests that any function $F \exp \{(2\pi ie/hc) \int \phi_m dx^m\}$ may be used as a scale factor, where F is a function of the coordinates, and, from the occurrence of ψ as the scale factor in our theory, we naturally turn to that function to see if it is of this form. The square of the length is equal to

$$\alpha^m A_m \alpha^n A_n,$$

L so that the invariant length would be expected to be L , where

$$L^2 = \alpha^m \alpha^n A_m A_n \psi = l^2 \psi.$$

but this is a matrix with four components $l^2 \psi_n$ and thus each component must satisfy the condition of invariance. Thus we have to examine whether ψ_n is of the correct structure.

If we turn to some of the problems treated we shall see that this is the case. Thus in the special case of an electron moving along the axis of x in an electrostatic field, we find that a solution is sought of the form $\psi = \psi_0 \exp \{(2\pi i/h) (px - Et)\}$,

where p is the momentum and E the energy. In this case, if the electrostatic potential is ϕ and we use the relativistic form, $E = (mc^2 + e\phi)$. This solution is a particular case of the general form

$$\psi = \psi_0 e^{\left(\frac{2\pi i}{h}\right) \int \Pi_n dx^n},$$

where Π_m is the generalized momentum introduced by Wilson and denotes $(p_m + ec^{-1} \phi_m)$. In the case considered $\Pi_4 = iE/c$, and $\Pi_1 = p$. It is clear that ψ is of the correct form, for it contains the required exponential factor.

But it is interesting to note that in this case we are neglecting any contribution to the change of length made by the factor

$$e^{\frac{2\pi i}{h} \int p_m dx^m}.$$

In other words we regard this quantity as if it were included in ψ_0 and, with it, had no influence on the metric. Since

$$p_m dx^m = m_0 g_{mn} \frac{dx^n}{d\tau} \frac{dx^m}{d\tau} d\tau$$

$$= -m_0 c^2 d\tau,$$

the expression becomes

$$e^{-\frac{2\pi i}{h} m_0 c^2 \tau}.$$

For the sake of symmetry we write

$$c\tau = x^5, \quad \frac{e}{c} \phi_5 = -m_0 c,$$

so that the factor becomes

$$e^{\frac{2\pi i e}{hc} \int \phi_5 dx^5}.$$

Thus if we had made use of a five-dimensional system the complete scale factor could have been written

$$e^{\frac{2\pi i e}{hc} \int \phi_\mu dx^\mu},$$

where the summation over μ is from 1 to 5.

In such a system of coordinates the fifth matrix α_0 would have been included in association with the fifth axis and would have appeared symmetrically with the other four.

It appears that the omission of $\exp(2\pi i/h) \int p_m dx^m$ is due to the use of only four coordinates and that this system allows something to escape from our scale factor. The use of the parallel displacement in association with the α^m restored the factor, but not with the same symmetry as that associated with a fifth coordinate.

The suggestion is that the scale factor should be used in the form given by

$$\psi_0 e^{\frac{2\pi i}{h} \int \Pi_n dx^n} = \psi_0 e^{-\frac{2\pi i}{h} m_0 c^2 \tau + \frac{2\pi i e}{hc} \int \phi_m dx^m},$$

and that each part is to contribute to the change of the length l , i.e. of the ordinary length, according to the formula

$$\frac{\delta l}{l} = -\frac{2\pi i e}{hc} \phi_m \delta x^m + \frac{2\pi i}{h} m_0 c^2 d\tau. \quad \dots(29).$$

§ 10. ON THE INTERPRETATION OF THESE RESULTS

We regard the existence of a definite change in the length of a vector, when it undergoes a parallel displacement, as associated with the presence of an electromagnetic field. This makes the first part of the change as represented by the first term on the right-hand side of equation (29) a physically observed quantity, which we observe as the electromagnetic field. But our ordinary measurements in space-time do not seem to take account of the second term, at any rate as a change in δl . The question is how we can account for this fact, since the term itself has a place in the quantum equation and thus corresponds to a physical quantity. We suggest that it escapes us because in all physical measurements we observe only changes in δl corresponding to a complete period in x^5 , i.e. our observations are on integral multiples of units of x^5 of magnitude h/m_0c . This being so $\exp \{(2\pi i/h)(mcx^5)\}$ always changes by unity and with reference to τ we can say that, in the observation of a particle, intervals of proper time less than h/m_0c^2 have no physical significance.

This principle of minimum proper time has been stated before⁽⁷⁾ and is in agreement in principle with the view expressed by Ruark⁽⁸⁾ that an element of absolute uncertainty exists in association with the location of a particle of magnitude h/mc . Many writers have made a similar suggestion and the fact that the conclusion is reached from many differing points of view seems to show that it is an expression of some physical law. It is interesting to note that in terms of ordinary space and time there is a lower limit to these elements respectively of $h\beta/m_0c\sqrt{(1-\beta^2)}$ and $h/m_0c^2\sqrt{(1-\beta^2)}$, where β is v/c . The meaning is that in the study of the track of a moving particle the accuracy of location is limited. When the velocity becomes very large the location is impossible and we cannot describe the motion as that of a particle, since some degree of location is associated with the concept of a particle. When v/c has the value $1/\sqrt{2}$ the value of the space limit is h/m_0c . Thus if we are studying the length of the track of a particle of this order of magnitude, the error is of the same order as the length itself when the ratio v/c becomes appreciable. Any conclusions drawn in such a case are therefore untrustworthy.

Some of these remarks have been made before, but the result has never been deduced in association with Dirac's equation. We have seen that it is closely associated with that equation, both being part of the same theory.

It seems clear that an element is missing from the quantum theory in its present form. The use of an exclusion principle and the occurrence of negative energy-states indicate the need of a new guiding principle as part of the theory. The derivation of the quantum equation and the interpretation of the change of length during a parallel displacement which has been given here are to be regarded as a search for a new feature. The principle of minimum proper time is itself of the nature of an exclusion principle, limiting the region of application of the quantum equation. The principle suggests that this equation must not be applied when the region is one where changes occur in a distance of h/m_0c ; in fact, it suggests that to speak of changes of this kind in association with particles does not correspond to

physical reality, when applied to cases of very rapid motion. This being the case our development of the equation shows it to be part of a theory which sounds a note of warning when we approach the confines of its domain.

It is interesting to note that in connexion with discussions on the probability of transitions to states of negative energy, Bohr has expressed the opinion that finite probabilities are to be expected when a change of potential of the order m_0c^2 occurs in a distance of magnitude h/m_0c . This expression of opinion has been verified by a calculation by Sauter⁽⁹⁾, who applied Dirac's equation to the problem.

REFERENCES

- (1) FLINT and FISHER. *Proc. roy. Soc. A*, **117**, 625 (1927).
- (2) LONDON. *Z. Phys.* **42**, 375 (1927).
- (3) FLINT. *Proc. roy. Soc. A*, **150**, 421 (1935).
- (4) MIMURA. *J. Sci. Hiroshima Univ. A*, **5**, 99 (1935).
- (5) EDDINGTON. *Mathematical Theory of Relativity*, 2nd ed. p. 218 (1930).
- (6) SCHROEDINGER. *Berl. Ber.* p. 105 (1932).
- (7) FLINT and RICHARDSON. *Proc. roy. Soc. A*, **117**, 630, 638 (1927).
- (8) RUARK. *Proc. nat. Acad. Sci., Wash.*, **14**, 322 (1927).
- (9) SAUTER. *Z. Phys.* **69**, 742 (1931).

NOTE ON THE THREE ABSOLUTE SYSTEMS OF ELECTRICAL MEASUREMENTS

BY THE LATE SIR R. T. GLAZEBROOK, F.R.S.

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IN dealing with electrical and magnetic problems we have, in the most general case, to consider three systems of forces between the quantities concerned. These are (1) forces between quantities of electricity, (2) forces between quantities* of magnetism and (3) forces between electrical currents and quantities of magnetism.

Each of these sets of forces can be expressed in terms of the electrical and magnetic quantities concerned, but such expressions will be arbitrary, depending on the arbitrarily selected units, in terms of which the quantities dealt with are defined and measured.

If we wish to make the measures absolute, i.e. to express them in terms of the "absolute unit" of force, that force which produces unit acceleration in unit mass, we must multiply the arbitrary values by suitable coefficients and there will be three of these corresponding to the three classes of force just enumerated. These coefficients are generally denoted by the symbols k_0 , μ_0 , and A . They are all arbitrary but their selection will define the units in terms of which our electrical quantities must be measured if we wish the forces between them to be measured absolutely.

Now the theory of dimensions shows us that the dimensions of $A^2/k_0\mu_0$ are those of the square of a velocity, while it follows from electrical theory that the velocity is c , the velocity of wave propagation. Thus $A^2/k_0\mu_0 = c^2$. (It is perhaps important to note that in 1868, when the absolute theory was being developed, this was not known.) It follows, therefore, that of the three coefficients any two can be treated as arbitrary and independent, and the third is then fixed. Moreover, our equations expressing (1), (2), (3) will be simplified if as many as possible of the coefficients are arbitrarily made unity.

Maxwell accordingly chose to make A equal to unity. It was then open to him to make either μ_0 equal to 1, when we have the electromagnetic system, or k_0 equal to 1, the electrostatic system. But there is a third alternative—indeed many more are possible; we can make both μ_0 and k_0 equal to unity. Then we are left with $A^2 = c^2$ or $A = c$. This is Gauss's system. These are the three most simple systems ordinarily employed, and all are direct consequences of the result that in the endeavour to express electrical and magnetic forces in absolute measure we necessarily introduce two arbitrary coefficients, to each of which we assign the value unity, as leading to the simplest and most direct relations between electrical

* We are generally agreed that a quantity of magnetism "is only another term for a distribution of electrical currents", but as Maxwell showed, it is useful, and for the present necessary, in the theoretical and mathematical development of the subject to retain the idea of a magnetic pole.

quantities and the fundamental units of length, mass and time. Each of the systems has its own use. We cannot say that any other system replaces the three systems now in use, namely the absolute electrostatic c.g.s. system, the absolute electromagnetic system and the practical series.

The first two systems are closely connected. Thus on the electromagnetic system we have

$$f = \frac{mm'}{\mu_0 r^2}; \quad f = \frac{qq'}{k_0 r^2}; \quad f = \frac{mids \sin \phi}{Ar^2},$$

with $\mu_0 = 1$ and $A = 1$.

But

$$A^2/\mu_0 k_0 = c^2,$$

$$\frac{1}{k_0} = c^2,$$

$$f = \frac{qq'c^2}{r^2} = \frac{cq \times cq'}{r^2} = \frac{\epsilon\epsilon'}{r^2};$$

i.e. if $\epsilon = cq$, $\epsilon' = cq'$, i.e. if ϵ and ϵ' are quantities of electricity measured in terms of a unit quantity which is $1/c$ of that in which q and q' are measured, and in a medium in which μ_0 is unity (free space) the quantities q , q' repel each other with a force which is exactly the same as that between the quantities ϵ , ϵ' in a medium in which k_0 is unity (also free space) when electrostatic units are employed.

Just as in some cases it is preferable to measure mass in kilogrammes, in others in milligrammes, so in some cases it is useful to measure electricity in terms of a unit which in free space repels an equal unit with unit force, in others it is desirable to employ a unit of electricity such that the force will be c^2 units of force.

Electrotechnicians find this last unit more convenient, but this method even when expressed in terms of some new system of units cannot replace the other.

APPENDIX A*

INTENDED SUBSTITUTION OF THE PRACTICAL ABSOLUTE SYSTEM OF ELECTRICAL UNITS FOR THE EXISTING INTERNATIONAL SYSTEM

Statement issued by the International Committee

After a revision in 1921 of the international treaty known as the "Convention du Mètre", under which at present thirty-two nations co-operate in the maintenance of the international prototype standards of the metre and kilogramme,

* Appendix A is a translation from the original French text of a series of resolutions approved for publication by the International Committee of Weights and Measures in October 1935. Appendices B and C relate to the question of the choice of the fourth (electrical) unit. The International Electrotechnical Commission, having recommended the adoption of the m.k.s. system of electrical units, known as the "Giorgi system", referred the question of the fourth unit both to the International Committee of Weights and Measures and to the S.U.N. Committee of the International Union of Physics for advice. Appendix B is a translation of resolutions dealing with this question approved by the International Committee of Weights and Measures for transmission to the I.E.C., and Appendix C is the reply of the S.U.N. Committee to the I.E.C. The three appendices together indicate the present position with regard to the intended eventual establishment of the system of practical electrical units on a self-consistent absolute basis.

authority was entrusted by the Conférence Générale des Poids et Mesures to the Comité International des Poids et Mesures in 1927 to take up also the question of electrical units. An advisory electrical committee, including representatives of the principal national laboratories, was appointed, and acting on the advice of this committee, the International Committee in 1933 recommended, and the Conférence Générale of that year approved in principle, the eventual substitution of the practical absolute system of electrical units for the present international system. The Conférence further instructed the Comité International to take the necessary steps to give effect to this decision.

At its meeting in October 1935 the Committee decided that the work on the subject which has been in progress for so many years in the various national laboratories had reached a stage at which it was possible to fix a date for the change, and authorized the publication of the following statement (translated from the original French text):

"1. In accordance with the authority and responsibility placed upon it by the General Conference of Weights and Measures in 1933, the International Committee of Weights and Measures has decided that the actual substitution of the absolute system of electrical units for the international system shall take place on the 1st January, 1940.

"2. In collaboration with the national physical laboratories, the Committee is actively engaged in establishing the ratios between the international units and the corresponding practical absolute units.

"3. The Committee directs attention to the fact that it is not at all necessary for any existing electrical standard to be altered or modified with a view to making its actual value conform with the new units. For the majority of engineering applications the old values of the international standards will be sufficiently close to the new for no change, even of a numerical nature, to be required. If for any special reason a higher precision is necessary numerical corrections can always be applied.

"4. The following table gives a provisional list of the ratios of the international units to the corresponding practical absolute units, taken to the fourth decimal place. Since differences affecting the fifth decimal place exist between the standards of the international units held by the various national laboratories and also because all the laboratories which have undertaken determinations of the values of their standards in absolute measure have not yet obtained final results, the Committee does not consider it desirable for the present to seek a higher precision. At the same

Table

1 ampere international	=	0.999 9 ampere absolute
1 coulomb	"	= 0.999 9 coulomb "
1 ohm	"	= 1.000 5 ohm "
1 volt	"	= 1.000 4 volt "
1 henry	"	= 1.000 5 henry "
1 farad	"	= 0.999 5 farad "
1 weber	"	= 1.000 4 weber "
1 watt	"	= 1.000 3 watt "

time it hopes that it will be possible to extend the table of these ratios with a close approximation to the fifth decimal place well before the date fixed for the actual substitution of the practical absolute system for the international system."

APPENDIX B

RESOLUTIONS*, RELATIVE TO THE CHOICE OF A FOURTH UNIT IN THE GIORGI SYSTEM, ADOPTED BY THE COMITÉ CONSULTATIF D'ÉLECTRICITÉ AT ITS MEETING IN SEPTEMBER 1935 AND APPROVED BY THE COMITÉ INTERNATIONALE DES POIDS ET MESURES

Resolution 5a, after a statement as to the dependence of the Comité Consultatif on the International Committee, continues:

"The Comité Consultatif considers that in the first place it should draw attention to the fact that an important majority among the members present expressed the opinion that the connexion between mechanical and electrical units should be secured by assigning the value 10^{-7} in a non-rationalized m.k.s. system, or $4\pi \cdot 10^{-7}$ in a rationalized system, to the quantity which is generally known as the 'permeability of space'.

"On attention being called to the fact that the form in which the question was put limited the choice to the seven practical units (coulomb, ampere, volt, ohm, henry, farad and weber), the Committee unanimously agreed that the only choice lay between the ampere, defined as being one-tenth of the c.g.s. electromagnetic unit of current, and the ohm, defined as 10^9 times the electromagnetic unit of resistance, these two quantities being consistent with the values 10^{-7} and $4\pi \times 10^{-7}$ indicated above for the permeability of space.

"Finally the Committee decided in favour of the ohm by the narrow majority of 4 votes against 3 for the ampere; one member did not vote."

Resolution 5b. This refers to a note presented by Mr Sears at the following Session of the Comité Consultatif which, it is recorded, "received the unanimous and favourable approval of the Comité who decided to transmit it (as part of their report) to the International Committee" by which it was subsequently approved, subject to possible small changes in detail. The text of the note is as follows:

"1. Electromagnetic theory leads to the relation $A^2 = \mu_0 k_0 c^2$ between the four quantities represented in the formula. Of these c is the velocity of propagation of electromagnetic waves in space; μ_0 the magnetic permeability of space; k_0 the inductive capacity of space (permittivity); and A a constant coefficient. To obtain a complete theoretical system of electrical units, the values of two of the three quantities A , μ_0 and k_0 , must be fixed independently. The third is then also fixed by the relation quoted above.

"2. The magnitudes of the electrical units of the system, the adoption of which

* Translated from the *Report* made by the Comité Consultatif to the International Committee of Weights and Measures.

was sanctioned by the Conférence Générale of 1933, are identical with those of the practical units derived from the classical c.g.s. system of Maxwell.

"3. These systems are based essentially on the conception of a constant value for the permeability of space, this value in Maxwell's system being numerically equal to 1. For the m.k.s. system, not rationalized, this permeability should have the value 10^{-7} , and for the m.k.s. system, rationalized, the value $4\pi \cdot 10^{-7}$. In each of these systems the coefficient A is taken as a numerical constant to which the value unity is assigned. Thus it does not appear again in the equations. The principal units of these two m.k.s. systems will then be the same as those of the practical system, the adoption of which has been sanctioned by the Conférence Générale of 1933.

"4. The various electrical units can all be derived from these conceptions by means of equations representing physical laws, and employing constants suitably selected. In principle no one of these units has priority over the others.

"5. The definitions adopted for the principal electromagnetic units might run as follows. (a) *Ampere*. The ampere is the constant current which, if maintained in two straight parallel conductors of infinite length at a distance of one metre apart in empty space, produces between these conductors a force equal to 2×10^{-7} m.k.s. units of force per metre length. (b) *Coulomb*. The coulomb is the quantity of electricity transported per second by a current of one ampere. (c) *Volt*. The volt is the difference of electrical potential between two points on a conducting filament carrying a constant current of one ampere when the power dissipated between these points is equal to the m.k.s. unit of power (watt). (d) *Ohm*. The ohm is the electrical resistance between two points of a conductor when a constant difference of potential of one volt applied between these points produces a current of one ampere in the conductor, provided that the conductor is not the seat of any electromotive force. (e) *Weber*. The weber is the magnetic flux which, when linked with a circuit of a single complete turn, would produce in that circuit an electromotive force of one volt if reduced to zero in one second at a uniform rate. (f) *Henry*. The henry is the inductance of a closed circuit in which an electromotive force of one volt is produced when the electric current in the circuit changes uniformly at the rate of one ampere per second. (g) *Farad*. The farad is the electric capacity of a condenser between the plates of which an electromotive force of one volt is produced when it is charged with one coulomb.

"6. These units may be derived as follows:

Ampere	I : ampere	I
coulomb	Q : ampere-second	IT
volt	E : watt per ampere	PI^{-1}
ohm	R : volt per ampere	EI^{-1}
weber	Φ : volt-second	ET
henry	L : volt-second per ampere	ETI^{-1}
farad	C : ampere-second per volt	$E^{-1}TI$

"7. For the current practice of laboratory measurements at least two primary reference standards are necessary and should be suitably chosen from among the

various units. The two reference standards should be the ohm and the volt of which the former is realized in the form of resistance coils; the latter in the form of Weston cells.

"8. For theoretical questions, such as the dimensional equations connecting the various units, the most convenient unit as a starting point for the derivation of the whole system of electromagnetic units appears to be the ampere, which is linked directly by simple relations both with the fundamental basis of the system and also with the other electric and magnetic quantities and which, moreover, has the advantage of eliminating fractional powers in the dimensional equations. From this point of view the ampere should be preferred as the fourth unit necessary to complete the m.k.s. system of electromagnetic units."

APPENDIX C

THE M.K.S. SYSTEM OF ELECTRICAL UNITS*

Reply from the S.U.N. Commission† of the International Union of Pure and Applied Physics to the request for advice on the choice of the fourth unit of the Giorgi system of units, contained in a letter dated June 27, 1935, to Prof. Abraham, Secretary of the International Union from Prof. Kennelly, Chairman of the E.M.M.U. Committee of the I.E.C.

The S.U.N. Commission has given very careful consideration to the request of the I.E.C. for help in the selection of the fourth quantity which, in the view of the I.E.C., is required to complete the m.k.s. system of units and desire to thank the I.E.C. for referring the question to the Commission.

The table which accompanies this reply has been prepared to show the relation between some of the quantities concerned in the m.k.s. and c.g.s. systems respectively.

The Commission has consulted a large number of leading physicists and, with hardly any exception, the following resolution, proposed by Dr Abraham, Secretary of the International Union of Pure and Applied Physics, has been approved.

"Considérant que lors de leur création les unités électromagnétiques du système pratique avaient été définies comme étant des multiples décimaux exacts des unités électromagnétiques c.g.s.

"Considérant que ces définitions initiales comportent plus de précision expérimentale et plus de sécurité que des définitions basées soit sur la conservation de certains étalons soit sur des techniques spéciales (colonnes de mercure, électrolyse).

* In the *Report* of the S.U.N. Commission approved by the International Union in October 1934 the value of B/H is given as μ_0 , not μ_0/A . The difference is due to the fact that in that proof it was assumed that $A=1$. If the symbol A is retained, the potential energy of a pole is $m\mu w/A$ and thus we obtain $B/H=\mu_0/A$.

† Sir Richard Glazebrook, President; Prof. Abraham (France); Prof. Kennelly (U.S.A.); Prof. Fabry (France); Prof. Keesom (Holland); Dr Ezer Griffiths, Secretary.

“La Commission émet l’avis;

“Il n’y a pas lieu de modifier les définitions initiales des unités électriques du système pratique, définitions qui fixent pour ces unités des valeurs égales à des multiples décimaux exacts des unités du système c.g.s. électromagnétique.”

The Commission are pleased to learn from a letter* from Prof. Marchant that at the I.E.C. meeting, although there is nothing in the minutes stating that the basis of the decision should be that the permeability of free space should be taken as unity, the reason why the question of the fourth unit was referred to the two Committees concerned was that the Commission was anxious that whatever was chosen should be consistent with the c.g.s. system of units. The table gives effect to this view. The S.U.N. Commission therefore recommend *that the table appended to this Report be accepted generally as defining the relation between the c.g.s. and the m.k.s. system of units.*

The accepted system of electrical measurements is based on the *Reports* of the British Association Committees on Standards for Electrical Measurements, 1861–70, 1880–1912. The Committee in 1863 decided to employ the absolute system of measurement which they explained in the following terms (p. 112):

“The word ‘absolute’ in the present sense is used as opposed to the word ‘relative’ and by no means implies that the measurement is accurately made or that the unit employed is of perfect construction; in other words it does not mean that the measurements or units are absolutely correct but only that the measurement, instead of being a simple comparison with an arbitrary quantity of the same kind as that measured, is made by reference to certain fundamental units of another kind treated as postulates.”

The fundamental units selected were those of length, mass and time. For the construction of standards of measurement the knowledge is required of the forces between electrical and magnetic quantities expressed in these fundamental units. Theory shows that, under the conditions assumed by Maxwell, one additional quantity is necessary, and is sufficient, to give us that knowledge. Theory also shows that this quantity, usually denoted by the symbol μ_0 , is a measure of the permeability, that is the ratio of magnetic induction to magnetizing force, in free space, the medium in which the measurements are supposed to be made. On the c.g.s. system the value of μ_0 is assumed to be unity. The m.k.s. system can be made absolute by the assumption of any convenient value for μ_0 , but if the units of that system are to be the practical units of the c.g.s. system the value† of μ_0 must be 10^{-7} .

In reply therefore to the request from the I.E.C. the S.U.N. Commission recommend *that the fourth unit on the m.k.s. system be 10^{-7} henry per metre, the value† assigned on that system to the permeability of space.*

* *Nature*, Lond., p. 110 (July 20th, 1935).

† On the rationalized system of units the value will be $4\pi \times 10^{-7}$.

Table showing the relation between quantities on the c.g.s. electromagnetic system and on the proposed m.k.s. system

	Length	Mass	Time	Magnetic coefficient μ_0	Electro-magnetic coefficient A	Space permeability μ_0/A	Coulomb	Ampere	Volt	Ohm
c.g.s.	1 cm.	1 gramme	1 second	1	1	1	10^{-1}	10^{-1}	10^8	10^8
m.k.s.	1 metre	1 kilogramme	1 second	10^{-7}	1	10^{-7}	1	1	1	1

On a modern Maxwell theory of electricity the permeability of space, which is measured by the ratio μ_0/A , is assumed to be a quantity having dimensions. Its value, therefore, will depend on the system of units employed. On the c.g.s. system the permeability of space has been selected as the unit of permeability. Hence on this system, since $A=1$, the value of μ_0 is unity. On the m.k.s. system the value of μ_0 is 10^{-7} , and on the rationalized m.k.s. system it is $4\pi \times 10^{-7}$.

At the same time the S.U.N. Commission desire to take this opportunity of placing on record their recognition of the fact that there are important electrical theories supported by a number of physicists in accordance with which $A=c$, the velocity of wave propagation, and $\mu_0 k_0$ is a pure number.

THE FOURTH UNIT OF THE GIORGI SYSTEM OF ELECTRICAL UNITS

BY THE LATE SIR R. T. GLAZEBROOK, F.R.S.

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IN a recent letter from Berlin, a valued correspondent, to whom I am indebted for much assistance in connexion with electrical units, sent me the following series of equations to show that "if in addition to the mechanical quantities one takes a single electrical quantity, for preference a quantity of electricity Q , it is possible to deduce all electrical quantities from this by means of a series of equations in each of which one and only one new electrical quantity appears". The question is discussed* more fully in Geiger and Scheel's *Handbuch der Physik*.

Equation	Quantity defined
$f = EQ$	E (field-strength)
$V = \int Edl$	V (voltage)
$Q = \int DdS$	D (displacement)
$I = dQ/dt$	I (current)
$f = I(lB)$	B (induction)
$\int Hdl = I$	H (field-strength)
$dI = kEdS$	k (conductivity)
$E = \frac{1}{K} D$	K (dielectric constant)
$B = \mu H$	μ (permeability)
$f = mH$	m (pole-strength)

My correspondent in a later letter emphasizes the fact that this is only given as an example. One might, he says, start from the equation $f = mH$ assuming m as the fourth unknown. In my reply I have expressed my general agreement with this as the basis of a mathematical theory of electricity and have suggested that in our correspondence we have had in view two different aspects of the matter. It is the purpose of this paper to explain the difference.

It was not the object of the British Association Committee in 1863 to establish the mathematical theory of electricity. Maxwell had that in view later when writing his book, and the equations quoted above are all, I think, to be found in that book. The existence of quantities of electricity, electric currents, etc., is assumed in such a theory, but this was not the *raison d'être* of the B.A. Committee in 1863. Its full title is the "Committee of the British Association for improving the construction of Practical Standards for Electrical Measurements". To do this it was necessary to have clear ideas as to the theory on which those measurements were

* Geiger and Scheel, *Handbuch der Physik*, 11, 10.

based, and the views of the Committee are set out by Maxwell and Fleeming Jenkin in Appendix C to the 1863 *Report*.*

It was the task of Maxwell and the B.A. Committee to develop a system which would enable them to construct apparatus—galvanometers, electrometers, ammeters and voltmeters we now call them—and resistance coils etc., for the determination of electrical quantities in absolute measure. The term “absolute measure” is explained in the *Report*. For this purpose the assumption of a fourth unit of the same fundamental nature as the units of length, mass and time, is not required and is misleading.

The series of equations given above, all of which are of course quite true, will not of itself enable us to construct a resistance coil or to set up apparatus for measuring currents and potentials. In the list f is the force (measured in terms of some definite unit of force, e.g. dynes) on a particle, a small sphere, carrying a quantity Q of electricity.

We can imagine this placed in a field of electrical force which is kept constant in time but varies from point to point of space. If we had the means of varying Q in a known manner and at the same time of measuring f at any given point of space we should find no doubt that the ratio f/Q remained constant and gave us the value of a quantity E which we denote as the electrical field-strength. By doing this at all points of space we could plot the field of force.

We come now to the second equation $V = \int E \cdot dl$. Before this is of any practical use to us we must know the relation between E and l , and we must be able to express both in terms of the coordinates of the point at which E is measured and integrate the result. To do this with any hope of success it is necessary to simplify the conditions. Suppose that the electrical charges are all measured in terms of Q_0 the fourth unit of the system; any charges may then be expressed as MQ_0 , NQ_0 etc., M , N etc. being numerics. If the field be due to a single charge MQ_0 concentrated at a point A we shall find of course that the force at a second point B is proportional to MQ_0 , and by varying the charge NQ_0 at the point B at which the force f is measured we can prove that the force is proportional to MNQ_0^2 , while by varying the distance r between the points A and B we can show that the force f dynes varies as MNQ_0^2/r^2 . Thus we may write

$$f = \frac{MNQ_0^2}{kr^2},$$

where k is a constant required to express as dynes the force MNQ_0^2/r^2 which is given in some arbitrary units.

Let us now suppose that the experiments have been conducted in a vacuum and that we can repeat them in some other insulating medium; we shall obtain a similar result but with a different value for the constant k . Thus k is a function of the properties of the medium in which the measurements are made and may be denoted as k_0 , k_1 etc. depending on the medium. But what we have done is simply to repeat Coulomb's experiments as extended by Faraday.

* Collected Volume of B.A. Electrical Standards *Reports*, p. 86.

Returning now to the vacuum we have

$$f_0 \text{ dynes} = \frac{MNQ_0^2}{k_0 r^2}.$$

Take the case in which M and N are each unity and r is 1 cm.—the assumed unit of length; then

$$f_0 = \frac{Q_0^2}{k_0}.$$

If further we prescribe that f_0 is to be 1 dyne, then

$$Q_0^2/k_0 = 1.$$

This equation can be satisfied by putting Q_0 and k_0 each equal to unity, i.e. by taking as our unit quantity of electricity that quantity of electricity which, in a field in which k_0 is unity, repels an equal quantity at a distance of 1 cm. with a force of 1 dyne. This, with the further assumption that k_0 is unity in a vacuum, is the definition of the electrostatic unit of electricity. The assumption that there actually exists a concrete fourth unit Q_0 which has this property is not necessary for our purpose. We may of course define Q_0 as the quantity which in a medium in which k_0 is unity repels an equal quantity at a distance of Q_0 centimetres with a force of 1 dyne, but we make no progress without some assumption as to the value of k_0 , the link which transforms into dynes the arbitrary units in which the force MNQ_0^2/r^2 is measured, and when that assumption is made it is superfluous to treat Q_0 as a fourth fundamental unit of the same kind as those of length, mass and time.

So far we have only considered an electrostatic problem. We may deal in a similar manner with the two equations $f = mH$ and $\oint H dl = I$. I is known from the equation $I = dQ/dt$, but unless we can express H and dl as functions of the co-ordinates of the point at which H and dl are measured we cannot proceed, and we find that, as above, we must introduce a quantity μ_0 , a function of the properties of the medium, in order to link up the unit of force, the dyne, with the arbitrary units in which m and H are measured. A third such link is required when we are dealing with the interaction between currents and magnetism involved in the equation*

$$f = I [lB].$$

This is usually denoted by the symbol A , and between the three we have the well-known relation $A^2/\mu_0 k_0 = c^2$, where c is the velocity of wave-propagation. The links are thereby reduced to two, A and μ_0 say. We cannot prescribe standards of measurement without assumptions as to these two quantities, and when these assumptions are made a fourth unit is not necessary for our purpose.

It is of course quite true that electrical theory assumes the existence of quantities of electricity, currents, magnets etc., and that the dimensional equations are simplified if expressed in terms of a quantity of electricity additional to those of length, mass and time, but the simplification of the dimensional equations was not the object of the B.A. Committee.

They set out to establish a set of standards for electrical measurements dependent

* The symbol [] indicates vector multiplication.

only on the three fundamental mechanical units, and by selecting as these fundamental units the centimetre, the gramme and the second, and assuming that in a vacuum the values of the two links A and μ_0 were each unity, they were able to do this and give us the c.g.s. system of practical units.

The same end is reached on the m.k.s. system if we assume for A and μ_0 the values 1 and 10^{-7} or on the m.k.s. rationalized system the values 1 and $4\pi \cdot 10^{-7}$. This is recognized by my correspondent, who, in his second letter to me, writes: "The Giorgi system is completely defined in the following statement: (1) the standards are M, K, S, μ_0 . (2) Three of its units agree fully with the standards M, K, S , a fourth unit is $10^7\mu_0/4\pi$; all other units can be derived from these by the principle of coherence. (3) If for any special case it is desired or is necessary to select four fundamental units from these, every man may make his choice according to his own preference."

If to this is added the statement that it has been assumed throughout that the value of A is unity and that therefore $\mu_0 k_0 c^2 = 1$ I agree entirely, but I prefer to consider μ_0 as a link and not a fundamental unit. I also agree that the discussion as to the value of A is a matter for electrical theory to consider, not for standardization.

It is perhaps of interest in conclusion to develop the consequences of a haphazard choice of four fundamental units.

Let us assume we take as these E , volts or electromotive force, P , power, T , time, and m quantity of magnetism. These are independent; we might equally well choose \bar{m} magnetic moment for m . Let L, M, F, W be dependent units of length, mass, force, and energy. By writing down the dimensional equations connecting these units with the four fundamental units—for instance $W = PT, F = W/L$ —we can proceed to find the dimensions of the other electrical and magnetic quantities including μ and k .

But this will not enable us to construct standards. To do this we must know the value we assign to μ and also, if electrostatic quantities are to be included, to k . We must distinguish between methods of measurements, *Messtechnik* in my correspondent's words, and the mathematical theory of electricity.

THE PROPERTIES OF HEUSLER'S ALLOY, AND THE TRUE SPECIFIC HEAT OF MANGANESE AND ITS DISCONTINUITY

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ABSTRACT. The physical properties of a sample of Heusler's alloy made in Prof. F. C. Thompson's laboratory at the University of Manchester have been examined. The experiments, which were always carried out on the same specimen, comprised determinations of density, intensity of magnetization, critical temperature, Curie's constant, electrical resistivity and its temperature coefficient, thermoelectric power and mean and true specific heat. A determination has also been made of the true specific heat of the metal manganese and a large discontinuity has been found about 350°C. , which is near to the critical temperature of Heusler's alloy. It was further found that the heat-capacity of the alloy is the sum of the heat-capacities of its constituents both below and above the critical temperature, thus following Regnault's rule, and the same rule can be applied to magnetite.

§ 1. INTRODUCTION

FERROMAGNETIC substances are so few in number that the discovery of Heusler's alloy made a welcome addition to the list. The fact that an alloy of manganese, aluminium and copper, metals which separately are non-magnetic, should be strongly magnetic is so remarkable that it makes the properties of this alloy well worth investigating.

Considerations of this kind prompted the initiation of a research on the magnetic, electric and thermal properties of the alloy, but since the research was begun a few years ago some experimental work on one or two divisions of the subject has been published by other investigators. Nevertheless what is now submitted not only serves as additional evidence for the conclusion of others but also supplies some information not comprised in their researches.

The results which are here given have, moreover, a unique feature inasmuch as they have all been derived from experiments on one sample of the alloy, and this removes any objection to the effect that the physical qualities which have been measured are not comparable on account of differences in the percentage composition or treatment of the alloy. It will not be necessary to refer at length to experimental details but the methods adopted and the results obtained are given in full.

The alloy upon which experiments have been made was kindly supplied by

Prof. F. C. Thompson and was made in his metallurgical laboratory at the University of Manchester. Its percentage composition is very approximately as follows:

Copper	59.2
Aluminium	17.6
Manganese	23.3
			<hr/> 100.1

These are nearly atomic proportions. In form it was a short stout rod, and there were also some fragments of irregular shape. The material as received was brittle and the rod accidentally falling on the floor broke into two pieces. These pieces were from 6 to 7 cm. in length and 1.32 cm. in diameter and weighed from 60 to 70 g. each.

The density, determined by two methods, was found to be 6.60 g./cm³, but at the conclusion of a long series of experiments in which the alloy had been repeatedly heated to a temperature as high as and above the critical temperature, it appeared to have become a little less and then stood at 6.56.

The properties of this alloy which have been examined are (i) the intensity of magnetization at saturation; (ii) the critical temperature; (iii) Curie's constant; (iv) the electrical resistivity and its temperature coefficient; (v) the thermoelectric power, more particularly in the vicinity of the critical temperature; (vi) the specific heat at air-temperature and at the critical temperature, and the discontinuity at the critical temperature.

§ 2. INTENSITY *I* OF MAGNETIZATION

I

One of the fundamental magnetic quantities to be determined and one of chief interest is the maximum intensity of magnetization. As the specimen was, in shape, a short stout rod the isthmus method described by Ewing was the most suitable and the one adopted for this determination.

The short rod was wound with a primary and two secondary coils and was closely fitted between the poles of a powerful electromagnet excited by a current of from 6 to 7 amperes, which was sufficient to magnetize the specimen to saturation. The induction was measured by suddenly withdrawing the alloy from the pole pieces and observing the consequent throw of the moving system of a ballistic galvanometer which had been carefully calibrated with a standard primary and secondary. The calculation of the induction requires a correction for the residual magnetism of the specimen, which however was small as the dimension ratio was small. An independent experiment was made which allowed the necessary correction to be made amounting to 121 lines per cm.² The maximum induction was then found to be 5412 lines per cm.² and the field 302 gauss, and from these facts it follows that the maximum intensity I_0 of magnetization, treated as magnetic moment per unit volume, is 416. It may also be calculated that the permeability at this high induction is a little more than 18 and the susceptibility 1.4.

I_0

A further experiment by a magnetometric method, whilst confirming the amount of the residual magnetism, at the same time allowed the critical temperature to be

determined. The alloy was heated gradually up to and beyond the critical point and readings were taken of the magnetometer. These showed but little change until near the temperature of 345°C. , but above this point a rapid loss of magnetism occurred which became nearly complete about 375°C. The point where the loss of magnetism was most rapid was 360° and this may be taken as the critical temperature. Several other experiments to be described later confirm this temperature as a critical one.

The alloy on cooling remained virtually non-magnetic down to 350°C. and then slowly acquired magnetism. There was evidence of large hysteresis with temperature which perhaps was due in part to the small dimension-ratio of the specimen, but this question was not examined further.

 θ

§ 3. THE CRITICAL TEMPERATURE θ

There are marked changes in other than magnetic properties which are generally found to take place in ferromagnetics near the critical temperature for magnetism, and it is probable that the temperature at which these changes take place is nearly the same for all. In no case are the changes absolutely abrupt, but the temperature at which they take place most rapidly may be considered to be the critical point in a critical region. We may group here the critical points from a consideration of several properties which exhibit distinctive changes at the magnetic critical temperature.

(a) The direct determination of the critical temperature for magnetism has already been mentioned and this temperature was estimated to be 360°C. (b) The temperature coefficient of electrical resistivity, as with iron and nickel, increases to a critical value and thereafter approximates to the normal rate. Experiments carried out on Heusler's alloy show that the critical point lies near to 356°C. , a temperature rather lower than what has been found above. (c) When a thermojunction of the alloy is heated, the regular progression of the thermoelectric power begins to change into a new direction at about 345°C. continuing to 385°C. , and the change is most rapid about 362° , after which at temperatures higher than 385° it resumes a more normal course. The rapid change at 360° may be regarded as a critical temperature. (d) The alloy exhibits the rapid increase of true specific heat with rise of temperature and abrupt fall at the critical temperature which is characteristic of ferromagnetics, and experiments show that a maximum true specific heat and discontinuity occur very close to 364° .

Collecting these results together we have for the critical temperature: From magnetic experiments (a) 360° , from electrical resistivity (b) 356° , from thermoelectric power (c) 360° , from specific heat (d) 364° . The mean of these is very nearly 360°C.

§ 4. CURIE'S CONSTANT

The difficulties of determining Curie's constant are very much reduced if a comparative method is employed. A preliminary theoretical examination showed that this constant would probably be of the same order as for nickel and so it was

decided to make a comparison with nickel, more especially as Curie's constant for nickel has been determined with considerable precision and is perhaps better known than that for any other ferromagnetic.

The apparatus was in all essential points a copy of the torsion balance devised and used by Pierre Curie. The torsion wire was of silver 0.2 mm. in diameter and was attached to a torsion head divided into 100 divisions. The lower end of the wire carried an arm to one end of which was fixed the carriage for the metal to be tested, the other end of the arm being weighted with a counterpoise. The holder for the specimen was a small thin-walled glass tube. To ascertain when the arm was brought to the fiducial position a pencil of light was projected on to a mirror fixed to the vertical axis of the moving system, and the reflected ray fell on a scale at a distance of a metre from the mirror.

The heating-coil, which was wound non-inductively and supplied with an alternating current, was fixed firmly between the poles of a strong electromagnet which was maintained at constant excitation. Lastly the temperature of the specimen was determined from the readings given by a thermocouple of platinum and platinum-iridium on a scale one metre from the galvanometer. The disposition of heating-coil, holder, thermojunction and electromagnet was in general as in Curie's well-known experiments⁽¹⁾.

Weighed fragments of nickel and of Heusler's alloy were tested in alternate series of experiments and values proportional to the product of the susceptibility and excess of temperature above the critical temperature were obtained for each metal.

If C_n and C_a are Curie's constant for nickel and the alloy and K_n and K_a the mass susceptibilities respectively at any temperature T , above the critical temperature θ , we have

$$\frac{C_a}{C_n} = \frac{K_a (T - \theta_a)}{K_n (T - \theta_n)}.$$

A number of concordant determinations gave the ratio of C_a to C_n as 152.0 to 184.5 for equal masses, which is equal to 0.824.

Weiss and Foëx⁽²⁾ found the Curie constant for nickel in mass units to be 0.00540; hence Curie's constant for Heusler's alloy is 0.00540×0.824 or 0.00445. If the density of the alloy is 6.60 the constant in volume units (cm^3) is 0.0294. The reciprocal R' of Curie's constant for Heusler's alloy is therefore 34.1. A small correction to this number may be made to allow for a slight paramagnetism of the glass holder, and the final result is 34.0.

§ 5. ELECTRICAL RESISTIVITY AND ITS TEMPERATURE COEFFICIENT

For the determination of the electrical resistivity of the alloy a fall of potential method was employed. The alloy was in the form of a stout rod and a current of about 4 amperes was passed through it, whilst the fall of potential between two points was compared with that across a standardized resistance in circuit with the

$C_n, C_a,$
 $K_n, K_a,$
 T

θ_a, θ_n

R'

alloy. Arrangements were made for the reversal of the current and pairs of readings were taken for different currents.

Observations taken in this way led to the value $83 \times 10^{-6} \Omega$. for the resistance between the two specified points 5.4 cm. apart. The sectional area of the alloy being 1.327 cm^2 , the resistivity is thus found to be 20.4×10^{-6} , that is, 20.4 microhms per centimetre cube at air temperature.

The variation of resistivity with temperature was next determined, and now the only change required was to embed the alloy in a sand bath which could be evenly heated by a row of Bunsen flames. A thermometer graduated to 410° C. in contact

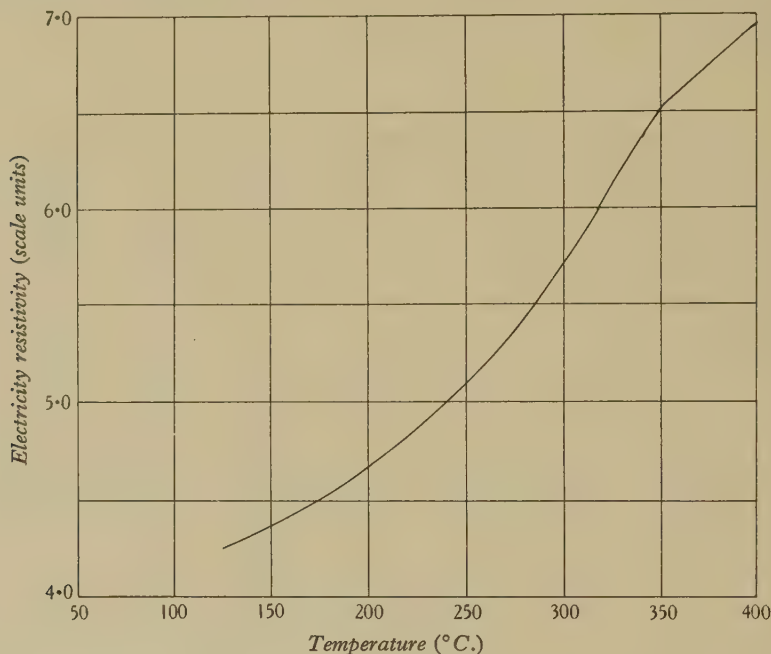


Figure 1. Electricity resistivity of Heusler's alloy.

with the alloy gave readings of the temperature which was slowly raised to 395° and as slowly lowered to the temperature of the room. The usual precautions were taken to eliminate thermo-currents and errors due to want of symmetry of the apparatus. The accompanying graph, figure 1, exhibits the results. When the alloy was heated the resistance increased, at an increasing rate, to between 350° and 360° C. at which point the rate of change became slower, and thereafter the increase of resistance was at a nearly constant but slower rate than at temperatures just below 350° . It is about 360° C. that the change per degree was most pronounced and this corresponds with the temperature at which magnetism is being most rapidly lost.

The temperature coefficient between 25 and 125° is 0.0016, which is comparable with other alloys but much less than for pure metals and very much less than for the pure magnetic metals.

O. Heusler's experiments⁽³⁾ on five samples of the alloy with different percentages of manganese, copper and aluminium show great variations in electric resistivity. They range from 76.2×10^{-6} to 15.8×10^{-6} at 20°C. , and the temperature coefficients at these extremes, referred to 20°C. , are 0.00166 and 0.00207 respectively.

A recent valuable research by Y. Matuyama⁽⁴⁾ on the magneto-resistance of magnetic metals for longitudinal magnetic fields at low and high temperatures includes among these metals Heusler's alloy and traces at the same time the curve of its resistivity and temperature. The alloy contained 70.39 per cent of copper, 12.27 per cent of aluminium and 17.34 per cent of manganese. The temperature coefficient of resistance between 0° and 100° was 0.00166, which agrees with the specimens of the alloy cited above; the rate of change of resistance increased rapidly towards 300°C. and thereafter became much less. Thus 300°C. appears to be the critical temperature.

It is shown that the negative value of the magneto-resistance, $\Delta R/R$, always increases with field strength in a longitudinal magnetic field, and the absolute value of $\Delta R/R$ is very large at low temperatures, but it decreases rapidly with rise of temperature and becomes zero from 290 to 330°C. Magneto-resistance is therefore a property characteristic of the ferromagnetism of the alloy and vanishes with its loss. Iron, nickel and cobalt are found to exhibit a similar behaviour in this respect, the magneto-resistance vanishing or becoming exceedingly small at the critical temperature.

§ 6. THERMOELECTRIC POWER

The thermoelectric power of iron and nickel shows a decided change in the neighbourhood of the critical temperature, a rapid augmentation taking place from less to greater positive values in iron and from greater to less negative values in nickel. It is therefore of interest to determine the behaviour of Heusler's alloy when it forms one of the metals of a thermoelectric couple. A junction of German silver and the alloy gave a suitably large e.m.f. on being heated and arrangements were made to work with this pair of metals.

The rod of Heusler's alloy was fixed with one end projecting into a lead box filled with cold water, which was kept flowing through the box at a rate which maintained the temperature constant; the other end of the rod in contact with the German silver was inserted in a hard glass tube on which a coil of high resistance wire was wound, the whole being jacketed with asbestos. The free end of the German silver wire was carried to a high-resistance galvanometer and the circuit was completed by connecting the second terminal of the galvanometer to the end of the alloy in the cold water.

Readings of the temperature of the hot junction were made by means of a nitrogen-filled mercurial thermometer graduated to 410°C. , but in some later experiments a platinum and platinum-iridium thermojunction was used. The various connexions throughout the circuit were carefully protected from accidental changes of temperature.

By gradually increasing the strength of the current through the heating spiral the hot junction was submitted to a slow uniform rise of temperature whilst the cold junction was steadily maintained at the temperature of the cold water. Preliminary experiments showed that some change in the regular rise of the thermo-

Table 1. Thermoelectric power of Heusler's alloy against German silver

Temperature (°C.)	Thermo-e.m.f. (μV.)	Thermo-electric power (μV./°C.)	Temperature (°C.)	Thermo-e.m.f. (μV.)	Thermo-electric power (μV./°C.)
100	575	4.76	375	2825	9.60
150	813	5.48	387	2940	10.40
200	1087	6.76	400	3075	11.45
250	1425	9.50	412	3212	13.60
300	1900	10.4	424	3375	15.90
312	2025	13.5	435	3550	20.00
325	2200	14.6	445	3750	21.20
337	2375	16.0	455	3962	23.70
350	2575	10.4	464	4175	25.00
362	2700	9.60	472	4375	

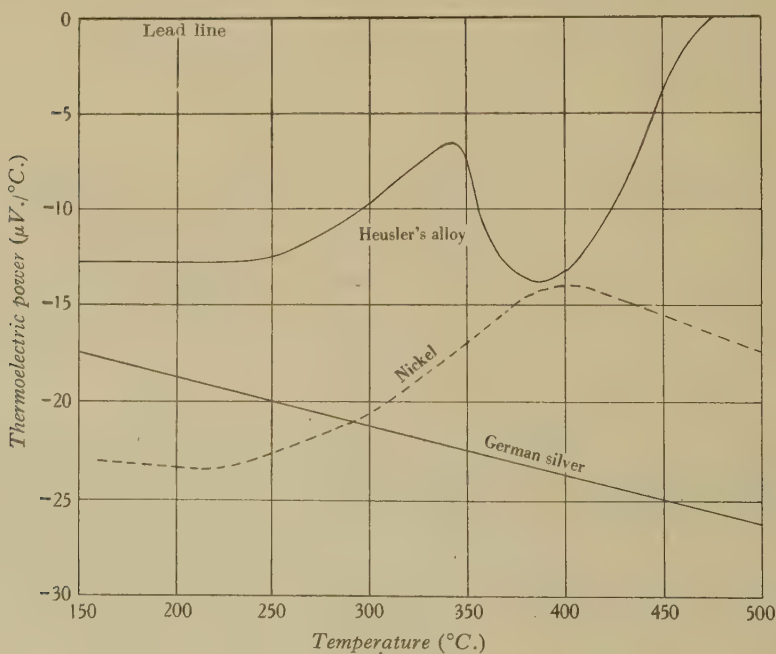


Figure 2.

electromotive force took place between 340 and 380° C. and subsequent careful observations, extending from the lowest to the highest temperatures, confirmed this. Table 1 gives the results arrived at with rising temperatures. German silver is strongly negative to lead and although the alloy is positive to German silver it is not

sufficiently so to make it positive to lead until temperatures approaching 500°C . are reached, as will be seen in figure 2, where the curve of thermoelectric power is traced relative to the zero line of lead which it crosses about 479°C . At higher temperatures than this the alloy no doubt becomes positive to lead.

The salient feature of the curve is the double inflection comprised between temperatures of 340 and 385°C .; the mid-temperature of 362° is close to the temperature which is the critical point for magnetism and where the discontinuity occurs in the specific heat.

In figure 2 the straight line representing the thermoelectric power of German silver relative to lead is drawn, and also, for the sake of comparison, the curve of thermoelectric power of nickel relative to lead. Nickel exhibits a change of 9 or 10 microvolts per degree in an interval of 200° , whilst the alloy performs an oscillation very little less, but in an interval of temperature of no more than 50° or 60° . The trend of the two curves is in opposite directions.

§ 7. THE SPECIFIC HEAT OF HEUSLER'S ALLOY

The specific heat of ferromagnetic substances exhibits features which are peculiar to such bodies. All the strongly ferromagnetic substances have an abnormal increase of the true specific heat with rise of temperature up to the critical temperature and at or near this point a brusque diminution to a lower value. This discontinuity has an interesting bearing on the theory of ferromagnetism.

Heusler's alloy when put to the test of experiment is found to conform to other strongly ferromagnetic bodies in the behaviour of its specific heat⁽⁵⁾. The experiments on the alloy here described were carried out by a calorimetric method. The alloy broken into small pieces was heated in a quartz tube round which was wound a spiral of high-resistance wire. The strength of the current passed through this spiral could be increased so as to raise the temperature of the interior of the tube to 500°C . or more if required. Both ends of the tube were closed but it was arranged that one end could be momentarily opened to allow the contents of the tube to be emptied into the calorimeter. During the heating the tube was kept in a horizontal position, but when the moment arrived for transferring the heated alloy to the calorimeter a swift movement turned the tube into the vertical position to let the alloy drop into the calorimeter. Temperatures were read on a thermocouple in the heater and on a finely graduated thermometer in the calorimeter. Thirty-nine experiments were made at different temperatures to determine the mean specific heat between the selected temperatures and about 15°C .

Table 2 and figure 3 show the mean specific heat. The accuracy of these measures only allows the fourth decimal place to be estimated, but this is more than sufficient to demonstrate the general conformity of Heusler's alloy to other ferromagnetics.

Table 2

Temperature ($^{\circ}\text{C}$.)	100	300	325	349	356	360	364	375	389
c_m	0.1170	0.1241	0.1265	0.1268	0.1297	0.1303	0.1308	0.1311	0.1316

A method due to Dumas, and used by Pierre Weiss⁽¹¹⁾, permits the calculation of the true specific heat to be made at any temperature. If c_m is the mean specific heat and C the true specific heat at temperature T then

$$C = c_m + \frac{dc_m}{dt} (T - t),$$

where $(T - t)$ is the interval of temperature used in calculating the true specific heat.

It is in the vicinity of the critical temperature that the true specific heat is of interest. Careful determinations near this point and calculations carried out according to the above formula give the true specific heat, at or just below the critical temperature, as 0.1786 and, just above, as 0.1426. The difference, ΔC , the discontinuity, is therefore 0.036.

Thus Heusler's alloy shows the same typical features as other ferromagnetics in the specific heat when the temperature rises to high values. Table 3 is given⁽⁶⁾ for comparison.

Table 3

Fe	Co	Ni	Heusler's alloy	Fe ₃ O ₄
C_θ ... 0.306	0.290 ⁽⁶⁾	0.158 ⁽⁷⁾	0.179	0.299
ΔC ... 0.120	0.118	0.032	0.036	0.079

§ 8. THE SPECIFIC HEAT OF MANGANESE AT HIGH TEMPERATURES

The specimen of manganese used in the following experiments had a purity of 98 per cent, the impurities being chiefly carbon and a little iron. It was hard, rather brittle and not readily acted upon by the air. Determinations of the mean specific heat between two temperatures were made by a calorimetric method and from such determinations the true specific heat was derived as described above in the section dealing with the true specific heat of Heusler's alloy. Twenty-five experiments were made and figure 3 traces the results obtained. Nearly all the points are averages of the results of two and three experiments between the specified temperature and 15° C.

The curve in figure 3 indicates very clearly that the mean specific heat of manganese treated as a function of the temperature suffers a sharp change in direction at about 350° C. and that there is at this temperature a large discontinuity in the true specific heat. It would appear from this that there is a critical temperature at 350° C.

The curve also shows that the true specific heat at this temperature is 0.274 and, just above, it falls abruptly to 0.149 which gives a discontinuity (ΔC) of 0.125. These are values of the same order as are found in iron.

The rapid rise of the true specific heat and the discontinuity at a critical temperature are all marked features of ferromagnetic materials, particularly the discontinuity which plays a leading part in the kinetic theory of ferromagnetism.

But the metal manganese unalloyed with other metals has never shown itself unequivocally ferromagnetic and the specimen used in these experiments has not exhibited any signs of strong magnetism. Nevertheless manganese united with one or with two other metals of a certain class forms alloys which in general show ferromagnetic properties, in some instances in a high degree, and this suggests that there is a ferromagnetism latent in manganese which can thus be made to exhibit itself. Bates and Pantulu⁽⁸⁾ have made a determination of Curie's constant for manganese

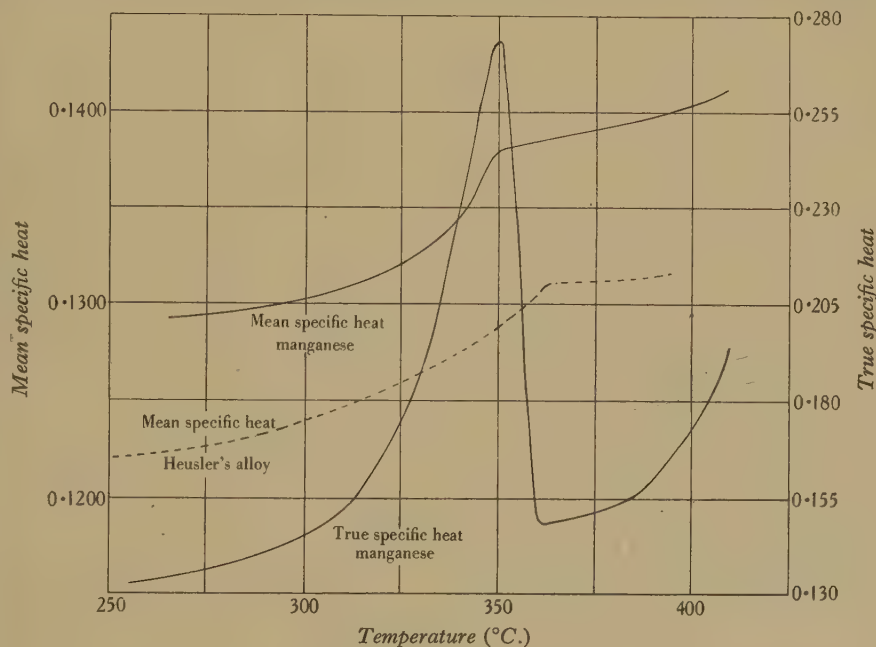


Figure 3. Mean and true specific heat of manganese.

and from this and other considerations the intensity of magnetization of the unalloyed metal may be expected to be of a high order, which would also be consistent with the large discontinuity in the true specific heat of the metal. But if future experiments finally decide that manganese is to be classed as non-ferromagnetic then the large discontinuity of the true specific heat of this metal may necessitate a revision of that part of the theory of ferromagnetism which attributes the discontinuity to the loss of an immense intrinsic magnetic field.

§ 9. THE HEAT CAPACITIES OF THE CONSTITUENTS OF THE ALLOY

The work of Neumann and Kopp and others has shown that the molecular heat of a compound can be treated as the sum of the atomic heats of its constituents and Regnault has extended the rule similarly to alloys. It is of great interest to apply this law to Heusler's alloy and to inquire whether the high true specific heat

of the alloy at its critical temperature is to be found in one or more of its constituents.

Beginning at air temperature we have the following values:

Table 4

	Percentage	Specific heat	Percentage heat
Copper	59.2	0.090	5.328
Aluminium	17.6	0.212	3.731
Manganese	23.3	0.122	2.843
	100.1		11.902

The calculated specific heat of the alloy is therefore 0.119. Experiments show it to be 0.117 which is in fair agreement with the calculation and is a confirmation of Regnault's rule. At the critical temperature of the alloy, the true specific heat of copper may be put at 0.113 and that of aluminium at 0.250 according to reliable determinations^(9, 10). The true specific heat of manganese should then be of the order 0.3 in order that the sum of the percentage heats of the constituents may be equal to the total heat of a hundred parts of the alloy, which, as has been shown above, is 17.86 calories for 100 g. at the critical temperature.

A determination of the true specific heat of manganese described above shows it to be 0.274 at 350° C. which is rather less than the estimated value of 0.3. Just a little higher than the critical temperature the experiment leads to 0.149 as the true specific heat which makes the discontinuity 0.125. Using these results we can now calculate the heat of a hundred parts of the alloy as follows:

At the critical temperature we have

	Percentage	True specific heat	Percentage heat
Copper	59.2	0.113	6.69
Aluminium	17.6	0.250	4.40
Manganese	23.3	0.274	6.38
	100.1		17.47

and just above the critical temperature

	Percentage	True specific heat	Percentage heat
Copper	59.2	0.113	6.69
Aluminium	17.6	0.250	4.40
Manganese	23.3	0.149	3.47
	100.1		14.56

These calculations make the true specific heat of the alloy at its critical temperature 0.175 compared with 0.179 by a direct determination, and just above the

critical temperature 0.146 compared with 0.143 from experiments on the alloy itself. The calculation assumes that manganese preserves its true specific heat when alloyed with other metals.

If magnetite be treated in the same way it may be shown that the very high true specific heat of iron of 0.306 at its critical temperature is preserved in the compound magnetite (Fe_3O_4) at its critical temperature. The truth of this is seen in the following table in which the composition is expressed in percentages. At the critical temperature we have

	Percentage	True specific heat	Percentage heat
Iron	72.3	0.306	21.91
Oxygen	27.7	0.275	7.62
	100.0		29.53

and just above the critical temperature

	Percentage	True specific heat	Percentage heat
Iron	72.3	0.186	13.45
Oxygen	27.7	0.275	7.62
	100.0		21.07

This calculation gives the true specific heat of magnetite at its critical temperature as 0.295 in comparison with 0.299 by direct experiment, and just above the critical point 0.211 as against 0.217 found from experiments on magnetite itself.

It appears that the high true specific heat of iron, which occurs in the pure metal at 785°C ., is preserved in the compound magnetite at its critical temperature of 580°C ., a temperature which is rather more than 200° below that of iron in the uncombined state.

REFERENCES

- (1) CURIE. *Œuvres*, p. 232.
- (2) WEISS and FOËX. *Arch. Sci. phys. nat.* **33**, 293 (1913).
- (3) HEUSLER, O. *Ann. Phys.*, Lpz., **19**, 155 (1934).
- (4) MATUYAMA. *Sci. Rep. Tôhoku Univ.* **23**, No. 4 (1934).
- (5) SUCKSMITH and POTTER. *Proc. roy. Soc.* **112**, 157 (1926).
- (6) ASHWORTH. *Phil. Mag.* **10**, 681 (Oct. 1930).
- (7) LAPP. *C.R. Acad. Sci.*, Paris, **186**, 1104-6 (1928).
- (8) BATES and PANTULU. *Proc. phys. Soc.* **47**, 197 (1935).
- (9) UMINO. *Sci. Rep. Tôhoku Univ.* **15**, 597 (1926).
- (10) GRIFFITHS. *Philos. Trans.* **213**, 119 (1913).
- (11) WEISS, PICCARD and CARRARD. *Arch. Sci. phys. nat.* **42**, 378; **43**, 22, 113 and 199.

DISCUSSION

L. F. BATES. I should like to point out that the use of the equation

$$C_a/C_n = K_a (T - \theta_a)/K_n (T - \theta_n)$$

postulates a linear variation of the reciprocal of the susceptibility with temperature for both nickel and Heusler alloy above their paramagnetic Curie points. Now it seems quite certain that a linear variation in the case of nickel does not exist in the temperature-range under consideration, and I do not know of any experiments which show a linear range in the case of Heusler alloy. Moreover, the temperatures θ_n and θ_a as defined by the author are not the paramagnetic Curie points which occur in the statement of the Curie-Weiss law, and θ_n should be replaced by a temperature some 15° higher, while θ_a should presumably be replaced by a temperature about the same number of degrees higher, even if approximately linear relations are assumed.

Bates and Pantulu, in measuring the susceptibility of amorphous manganese, did not make measurements above 350°C. , but they found no evidence of a marked break in the magnetic properties at 350°C. It therefore appears to me that some change in structure at 350° occurred in the case of the authors' specimen of manganese, and here X-ray data would help. The conclusions in the final portion of the paper appear to me to be based on an incomplete survey of the available data, for the results obtained with manganese arsenide are certainly not in agreement with them.

AUTHOR'S reply. The points referred to by Dr Bates in connexion with Curie's constant have not been overlooked, but there seems to be some divergence of opinion on the methods of obtaining the constant following the Weiss modification of the Curie law. Certain considerations, however, lead to a calculated value which is not far from that in the paper and which makes it acceptable.

Dr Bates's interesting and valuable researches on manganese arsenide do not invalidate what has been set out in the final part of the paper, but show that this substance has a behaviour all its own.

ON A NEW TYPE OF ELECTRONIC OSCILLATOR TUBE WITH PARALLEL PLANE GRIDS

By W. A. LEYSHON, PH.D., F.INST.P.

Received October 18, 1935. Read February 21, 1936

ABSTRACT. The paper describes results obtained with an experimental tube, the electrode system of which consisted of two parallel plane grids with two symmetrically arranged cathodes external to them. When Lecher wires were attached to the two grids, oscillations could be obtained either (A) with the tube used as a triode, potentials being applied to the grids in the usual way for the production of Barkhausen-Kurz oscillations, or (B) with both cathodes emitting and the two grids at the same positive potential. The longest waves generated with the B connexion satisfied the relationship $\lambda^2 v_g = \text{constant}$.

For both A and B the wave-lengths of the generated oscillations were determined almost entirely by the length of the attached Lecher wires.

The behaviour of the B system showed some resemblance to that of a relaxation oscillator maintaining, and coerced in frequency by, a vibrator of small damping.

§ 1. INTRODUCTION

SOME time ago Dr Eccles suggested to me that it might be possible to produce electronic oscillations in a tube having electrodes arranged as shown diagrammatically in figure 1.

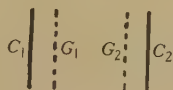


Figure 1. C_1, C_2 cathodes; G_1, G_2 grids.

C_1, C_2 represent two cathodes outside two plane electrodes G_1, G_2 to which a positive potential could be applied. The electrodes G_1, G_2 being of grid construction, space charge would accumulate in the otherwise field-free region between them, and oscillations should be maintained in a suitable Lecher wire circuit attached to the two grids.

A tube was made up and tested in March 1934. Lately, experiments have been made with a view to repeating and extending the results then obtained, a demountable Pyrex tube with movable electrodes being used. It was originally intended to defer the publication of the results given in the present paper until they had been verified and amplified with this new apparatus. However, work has been recently carried out on a plane-electrode demountable triode⁽¹⁾, some of the results of which appear to accord with those I obtained by using the original double grid tube as a triode. It seems likely to be of interest, therefore, to record now the behaviour of the double-grid tube, used both as a triode and in the manner for which it was in the first place designed.

§ 2. DESCRIPTION OF APPARATUS AND PROCEDURE

The arrangement of the electrodes in the experimental tube is shown in figure 2.

The cathodes consisted of W-shaped filaments of tungsten wire kept taut by small spirals of molybdenum wire, in quartz frames. The latter were held in position by the lead-in wires.

The grids, of copper gauze with a transparency of 50 per cent, were also supported by stout copper leads and the platinum-glass seals. The cathode connections were led out of the glass envelope on the opposite side from the grid leads, both sets of leads being horizontal.

The apparatus was connected through wide tubing, fitted with a large tap, to a Metropolitan-Vickers oil condensation pump, backed by a Hyvac pump. Apiezon

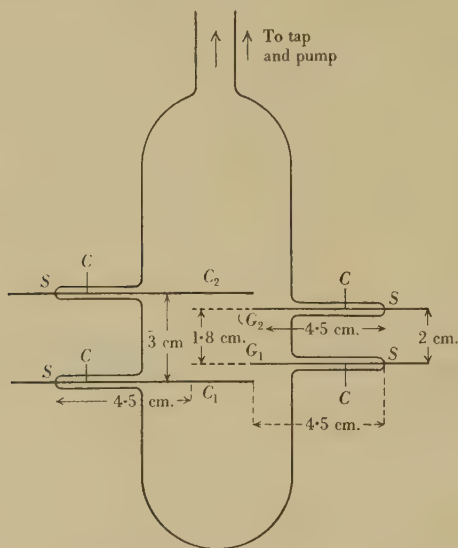


Figure 2. C_1 , C_2 cathodes; G_1 , G_2 grids (copper gauze 2 cm. square); S , S platinum-glass seals; C , C copper leads.

L grease was used for the tap, and for sealing the flat ground-glass-steel joint at the top of the pump.

The tube was baked out at 160° C. and the filaments were electrically heated while pumping proceeded. This treatment was repeated until the tube, itself used as an ionization gauge, showed little or no trace of residual gas. Before experiments were made on any particular day, the glowing and pumping-out processes were continued until consistent and repeatable results were obtained in determining the tube characteristics. The plot of log (grid current) against log (grid voltage) then showed a slope of $\frac{3}{2}$, with sufficient filament emission.

It was found that with a Lecher-wire system of suitable length attached to the two grids, and with one emitting cathode, Barkhausen-Kurz oscillations could be obtained with the greatest ease. These oscillations were utilized to heat the grids and remove traces of residual gas. The Lecher-wire system connected to the two

grids consisted of two parallel wires of stranded phosphor bronze, soldered at one end to two short copper pins passing through and firmly held by two vertical ebonite pieces supported by a wooden block. This block was fixed on a wooden baseboard along the edges of which two wooden strips were fastened to form a groove. The copper pins were at the same horizontal level as the leads from the two grids, and were soldered directly to the platinum wires leading out through the tube extensions. The phosphor-bronze wires passed through two holes in a copper plate about 8 in. square, which was supported in another wooden block which could slide in the groove. The holes were partially blocked by ebonite rings, with small copper tubes fitted through them. A blocking condenser was connected to the two tubes. The Lecher wires passed through these tubes, making contact with them, and then through holes in an ebonite piece fastened vertically on a third wooden block which was fixed to the baseboard. The effective length of the Lecher-wire system was altered by movement of the block carrying the condenser bridge and reflecting plate.

A Lecher-wire system could also be connected to the two cathodes when desired. In general, however, the positive ends of the cathodes were connected through a $0.003\text{-}\mu\text{F.}$ condenser, the negative ends being connected directly to each other.

§ 3. EXPERIMENTAL RESULTS

(A) *Tube used as triode.* Either triode (one cathode emitting) would oscillate very easily when the nearer grid was made positive and the outer grid was at some potential near that of the cathode. Oscillations for given values of inner grid voltage v_{g1} and outer grid voltage v_{g2} occurred over quite a large range of Lecher-wire length. For example, with v_{g1} equal to 160 V., v_{g2} equal to -2 V., and i_{g1} equal to 2 mA., oscillations occurred over a range of Lecher-wire length, measured from the middle of the electrode system, of $100 \rightarrow 24$ cm. When the Lecher-wire bridge was pushed steadily in towards the tube the amplitude at first increased, then suddenly dropped to zero at one particular point, and afterwards rose again.

It was observed that the current to the positive grid was always diminished when oscillation set in; in general this diminution was much greater than the resultant current to the outer electrode.

In one series of experiments, the Lecher wires connected to the grids were kept at a constant length of 63 cm. and it was found that the generated wave-length did not vary by as much as 2 per cent from the value 3.02 metres, although oscillations could be detected with v_{g2} varying from -6 to $+2$ V., and v_{g1} from $+98$ to $+184$ when $v_{g2} = -2$. The triode was working on the steep part of the $\{v_{g1}, i_{g1}\}$ curve, but nearer the top than the bottom bend.

With v_{g2} equal to -2 , as also with v_{g2} equal to $+2$, the oscillation-intensity, as measured by the deflection of the galvanometer in the wave-meter circuit at resonance, increased steadily with increase of v_{g1} .

In another set of experiments, in which a Lecher-wire circuit was attached to the two cathodes, the optimum position of the bridge on the grid side was

independent of v_{g1} and v_{g2} over a considerable range. The position was affected appreciably by the filament emission.

(B) *Tube used with v_{g1} equal to v_{g2} and both cathodes emitting.* It was found that oscillations could be obtained with this arrangement only when the vacuum in the tube was very good. It was necessary to pump out the tube for some time, and advisable to heat the electrodes by generating high-frequency oscillations with the A form of connexion before making the experiments.

In favourable circumstances oscillations of very good amplitude could be obtained with the two grids at the same positive d.-c. potential. The tube generated oscillations best when the emission currents from the two cathodes were equal. In all cases the onset of oscillation was accompanied by a diminution in both grid currents.

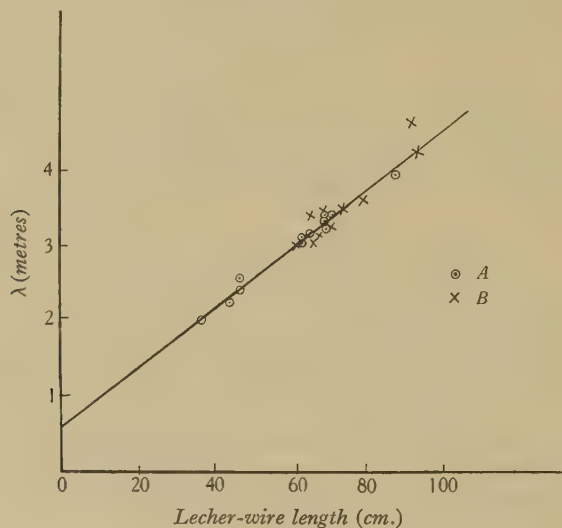


Figure 3.

In general, for fixed values of grid-potential and filament emission the range of Lecher-wire length for which oscillation would occur was very much smaller than for the A connexion. When the Lecher-wire length was steadily diminished the amplitude of oscillation increased and then abruptly stopped, and oscillations could not be restarted by further reduction of the effective Lecher-wire length.

When oscillations of large amplitude were being generated, it was sometimes found that touching either of the grid leads stopped the oscillations. They could be restarted by breaking and then re-making the connexion of the h.t. battery.

In figure 3 is shown the linear relation between Lecher-wire length (measured from the middle of the electrodes to the bridge) and the generated wave-length, for A experiments in which $v_{g1} \neq v_{g2}$ as well as for B experiments in which $v_{g1} = v_{g2}$. Figure 4 shows the relation between the wave-length generated and the voltage in case B. The wave-lengths were measured by means of a long Lecher-wire wave-meter, with crystal detector and galvanometer⁽²⁾ or by means of an absorption

wave-meter⁽³⁾. Other wave-lengths for the B arrangement were determined from a graph of $\{v_g, L\}$, figure 5, where L represents length of Lecher wires measured from the middle of the electrodes to the bridge, and from the $\{L, \lambda\}$ graph of figure 3. This procedure was justified by the results of experiments in which the Lecher-wire length was kept constant. For example with a Lecher-wire length of 94 cm. v_g could be changed from 148 to 176 V., i.e. over the whole range of v_g for which oscillation occurred, without producing any detectable change in wave-length.

Notes on the results. It was not possible, owing to the final puncturing of the glass envelope, to make a complete comparison between the behaviour of the tube when used in the A or in the B manner; however, with other circuit conditions the

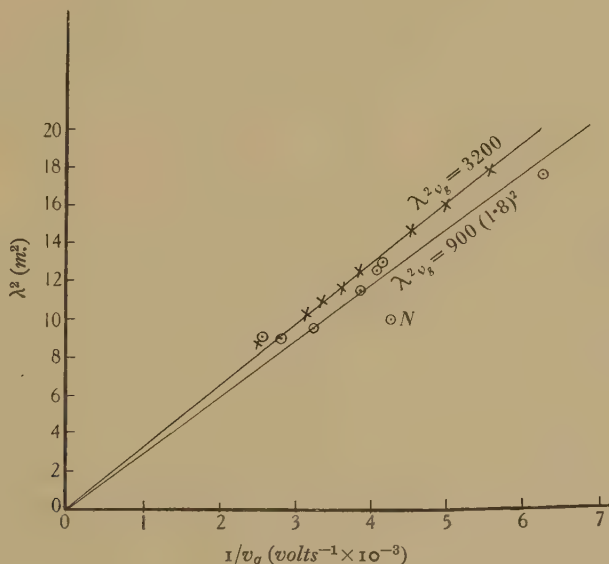


Figure 4. Points \times are from figures 3 and 5.

same, both cathodes emitting, and a definite value for v_{g1} , changing over from the B method to the A method ($v_{g2}=0$) involved shortening the Lecher-wire length for maximum oscillation—i.e. oscillations of longer wave-length were more readily maintained with the B arrangement. With the A connexion, oscillations were obtained when the grid current was limited either by space charge or by emission; with the B connexion, oscillations started when the grid currents were just emission-limited. It will be seen from figure 4 that all points except those corresponding to non-restoring conditions lie near the line for which $\lambda^2 v_g = 900 (1.8)^2$. This relation gives the wave-lengths calculated from $\lambda = 2cT$, where λ is the wave-length in metres, $c = 3 \times 10^8$ m./sec., and T the time of transit between G_1 and G_2 assuming a virtual cathode halfway between G_1 and G_2 , and full space charge. It is not certain, however, that these conditions actually held for the experiments; further work is desirable to clear up this point. It was found that the Lecher-wire circuit

between G_1 and G_2 was much more critically effective in controlling the frequency of oscillation than an additional Lecher-wire circuit between the two cathodes.

The results show the possibility of obtaining electronic oscillations with a new arrangement—a Lecher-wire circuit connected to two plane grid-form electrodes initially at the same positive potential and capable of collecting electrons from two symmetrically arranged external cathodes. The mechanism of maintenance has not

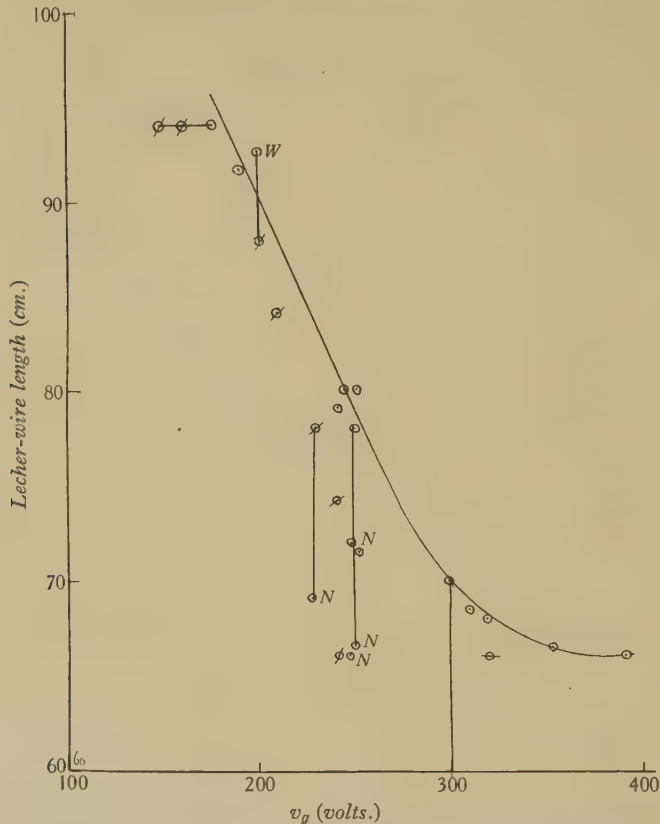


Figure 5. Lines show range of oscillation. ○ good amplitude, restoring; ⊙ N non-restoring; ⊗ not tested as regards restoring conditions; ⊗ W very weak oscillation.

yet been fully determined, but the results suggest that the effective oscillation of electrons is between and just beyond the two grids.

It is perhaps significant that in many experiments it was observed that the strongest oscillations were obtained for non-restoring conditions, and for the shortest possible lengths of Lecher wire, the circuit being otherwise unchanged. There appears to be some analogy between this result and the coercing of a relaxation oscillator by a coupled vibrator of small damping, like that which occurs, for example, in the neon-lamp tuning-fork circuit^(4,5).

§ 4. ACKNOWLEDGMENTS

I should like to express my thanks to Dr W. H. Eccles for suggesting the work and for his interest in its progress.

The experiments were carried out in the Physics Laboratory of the London (R.F.H.) School of Medicine for Women. My thanks are also due to the Council of the School for a grant from the Waller Research Fund for the purchase of apparatus.

REFERENCES

- (1) CHIPMAN, R. A. *Proc. phys. Soc.* **47**, 263, 1042 (1935).
- (2) CHAPMAN, F. W. *Wireless Engr.* **8**, 500 (1932).
- (3) MOORE, W. H. *Electronics* (November 1933); *J. Franklin Inst.* **217**, 347 (1934).
- (4) ECCLES, W. H. and LEYSHON, W. A. *Electrician*, **97**, 65 (1926).
- (5) LEYSHON, W. A. *Phil. Mag.* **4**, 305 (1927).

DISCUSSION

DR L. HARTSHORN asked whether the author had any clue to the reason why oscillations occur under the conditions described.

LORD RAYLEIGH asked what would be the effect of an extraneous magnetic field.

AUTHOR'S replies. In reply to Dr Hartshorn: An explanation of the method of maintenance of the B oscillations must take into account the following facts: (1) the grids were at or near a potential antinode of the oscillations in the Lecher-wire system (see figure 3); (2) oscillations began when the grid currents were just emission-limited, and both grid currents were diminished at onset of oscillation; (3) for a given value of the static potential applied to G_1 and G_2 , oscillations could be obtained over a considerable range of Lecher-wire length, and the generated wavelength was determined by the latter; for the longest waves generated $\lambda^2 v_g$ had a value which corresponded with the relation $\lambda = 2cT$, where T was equal to the time of transit of an electron either from G_1 to G_2 under full space-charge conditions, or from F_1 to F_2 with full space charge between F and G , and negligible space charge between G_1 and G_2 . It seems probable that the modes of maintenance of the A and B oscillations may be similar in nature; in each case two electron streams travel in opposite directions, and it may be supposed that periodic changes in electron-density either initiated or intensified by the variations of potential of G_1 and G_2 arrive at these electrodes in the appropriate phase for maintenance of oscillation. For case B the source of these periodic changes in electron-density is not likely to be a succession of pendular oscillations of groups of electrons between the two cathodes, since the effective grid-transparency would be only 25 per cent, being 50 per cent for each grid.

The present results do not enable one to discriminate completely between two other possible methods of maintenance: (a) Negative-conductance effects due to

the transit times of disturbances in the electron streams in the paths C_1 , G_1 , G_2 and C_2 , G_2 , G_1 respectively. The time of transit from G_1 to G_2 should, in this case, be equal to approximately one-half, and that from F to G approximately one-quarter, of the periodic time of the Lecher-wire oscillations. (b) A periodic supersaturation with space charge of the G_1 , G_2 space, with successive discharges in the G_1 and G_2 directions respectively. The interval between successive discharges would be equal to half the periodic time of the Lecher-wire oscillations. The fact that the periodic disturbances in the electron streams can be coerced over such wide frequency ranges (see figure 5) suggests that they are probably of relaxation rather than of sinusoidal form.

In reply to Lord Rayleigh: The effect of a magnetic field on the generation of oscillations by the original tube was not tried. Apart from the use of an axial magnetic field in the generation of electronic oscillations by the cylindrical diode used as a magnetron, it has been shown by a number of experimenters that the effect of such a magnetic field on the oscillations generated by commercial triodes in the usual Barkhausen-Kurz circuit is to produce effects similar to those brought about by a decrease of the plate potential. If either of the tentative explanations given in the preceding paragraphs of the mode of generation of the B oscillations is correct, the presence of a transverse magnetic field might be expected to hinder or stop oscillation, since no reversal of electron-path is supposed to occur in the absence of a magnetic field. A longitudinal field would have a focusing effect on the electron streams. Some electrons not initially travelling parallel to the axis of symmetry of the electrode system would spiral about the magnetic lines, and therefore would remain for a longer time between the electrodes. These would increase the normal space-charge density and might favour the production of oscillations if explanation (b) is the correct one. I hope in the future to try the effect of an extraneous magnetic field on another experimental tube with an electrode system similar to that of the original one, and generating oscillations in the same way.

THE VARIATION OF DOUBLE REFRACTION IN CELLULOID WITH THE AMOUNT OF PERMANENT STRETCH AT CONSTANT TEMPERATURE AND AT DIFFERENT TEMPERATURES

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Communicated by Dr R. E. Gibbs December 10, 1935. Read in title March 6, 1936

ABSTRACT. Different specimens of celluloid (xylonite) were stretched beyond the elastic limit, so that they had produced in them amounts of permanent stretch which differed from one specimen to another. The residual double refraction at constant temperature was measured in each specimen at a number of wave-lengths in the visible spectrum, and the dispersion in every case was found to follow the law $n/\lambda^2 = A - B\lambda$, where n is the permanent double refraction in wave-lengths at the wave-length λ and A and B are constants for the particular specimen. It was found also that in each specimen n had a maximum value at some wave-length λ_M , the values of λ_M being less in those specimens which had smaller permanent stretches than in those which had larger permanent stretches. Observations were made on the effect produced on the dispersion and on the values of λ_M by increase of temperature.

§ 1. INTRODUCTION

SOME years ago, S. R. Savur⁽¹⁾ showed that the dispersion of the residual double refraction in celluloid produced by permanent stretch changes with the amount of such stretch, and becomes increasingly anomalous as the permanent stretch increases.

Earlier than this, however, M. Wachtler⁽²⁾ had carried out a series of experiments in which he found that the residual double refraction changes sign as the permanent stretch increases. No such change of sign was observed by Savur, and considerable doubt was expressed by him as to the accuracy of Wachtler's work. Similar doubt was also expressed by Ramspeck⁽³⁾, but Wachtler later denied that any inaccuracy had occurred in his work. He stated however that he used a celluloid having a large content of camphor. Quite recently Derksen and others⁽⁴⁾ have investigated the change in the double refraction of celluloid with variation of camphor-content. Their results show that for celluloid in which the camphor-content is less than about 35 per cent the double refraction produced by overstrain is entirely positive, whilst for celluloid with a camphor-content of more than 40 per cent such double refraction is entirely negative. For one particular case, however, in which the camphor-content was exactly 40 per cent—the same as that used by Wachtler—the double refraction is positive for small overstrain, while for large

overstrain it is negative. The change of sign occurs for a stretch of about 8 per cent. Now the celluloid used by Savur had a camphor-content of about 24 per cent.

Hence it would appear certain that Wachtler and Savur were both right in their results, and the apparent discrepancy can be fully explained by the fact that they were using specimens of celluloid containing widely different amounts of camphor.

The present research was undertaken to find firstly the actual law of dispersion of residual double refraction in permanently overstrained celluloid, and secondly what change if any is produced in this dispersion by change of temperature. The celluloid used throughout was supplied by the British Xylonite Co., Ltd., and has the same camphor-content as that used by Savur, namely 24 per cent.

§ 2. PREPARATION OF THE SPECIMENS

Each specimen, cut from a sheet of xylonite 7 mm. thick, was of the approximate dimensions shown in figure 1. When the specimen was put under tension, a uniform stress was produced in the central portion *CD*. Throughout the parts *BC* and *DE* the stress changed fairly rapidly, and in the parts *AB* and *EF* it became quite small towards *A* and *F* except very near the holes where the load was applied. Each specimen was then placed in turn in the straining apparatus shown in figure 2. The knife-edge *A* being fixed, tension was applied by raising *B* until the desired amount of double refraction was produced in the centre of the specimen. As the specimen stretched, *A* and *B* both remaining fixed,

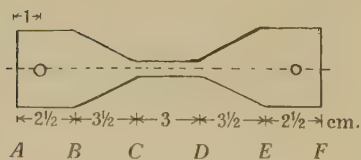


Figure 1.

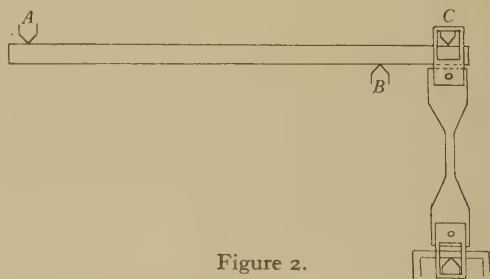


Figure 2.

the tension automatically decreased and hence *B* had continually to be raised to maintain the double refraction as required. In cases where a high residual double refraction had to be produced the tension had to be applied continuously for several weeks, and hence any risk of breakage during the times when the specimen was not under observation was reduced to a minimum by this method.

After release of the tension the specimen was left for several years, so as to ensure that all time creep in the residual double refraction had either ceased altogether or at any rate become negligible when placed between crossed nicol prisms in sodium light; the specimen then had an appearance similar to that shown in figure 3.

The numbers 0, 1, 2, ... refer to the order of the respective double-refraction bands. Thus the integral part of the residual double refraction in the central

section of each specimen could easily be determined merely by counting these bands.

Altogether seven specimens were prepared in this way, having at their central sections residual double refractions varying respectively from about 0.4λ to 7λ (at $\lambda = 5896$).

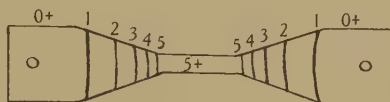


Figure 3.

§ 3. METHOD OF EXPERIMENT AT CONSTANT TEMPERATURE

The method used was the improved spectroscope method⁽⁵⁾. A preliminary set of observations had shown that an observable shift of the bands in the spectroscope was produced by a change in temperature of 1°C . in the specimen, and also by a change of 3°C . in the temperature of the quartz plate. It was therefore neces-

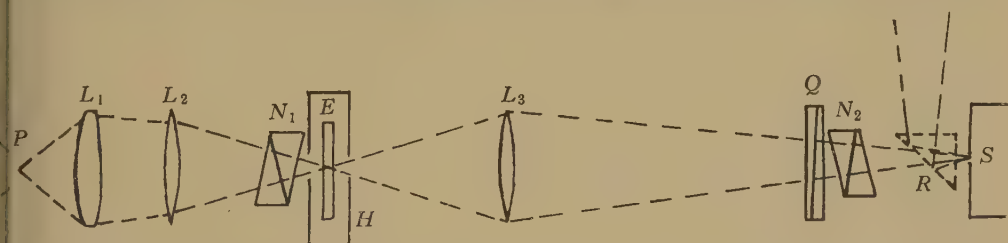


Figure 4. *P*, Point-o-lite; *N*₁, *N*₂, nicol prisms; *H*, heater; *L*₁, *L*₂, *L*₃, lenses; *E*, specimen; *Q*, quartz plate; *S*, slit of spectrograph; *R*, prism (removable) for iron spectrum.

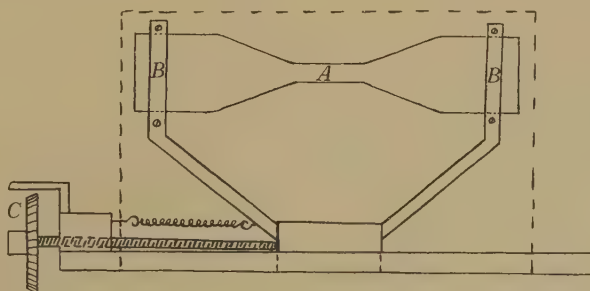


Figure 5. *A*, specimen; *BB*, clamps holding specimen; *C*, micrometer screw head.

sary to take precautions to keep the temperatures of both specimen and quartz plate constant within these limits. Moreover, as was to be expected from the nature of the material even in the central section of the specimen, the residual double refraction was found to vary slightly from point to point. An enlarged image of the central section was therefore produced on the slit of the spectroscope by means of a suitable lens system, the arrangement of the apparatus being as in figure 4. The specimen was mounted rigidly as in figure 5, and together with

its support it was entirely enclosed in a small electric heater so that it could be maintained at any desired temperature. By this means errors due to any movement of the specimen or change in its temperature during the progress of a set of observations were avoided. The time taken for each set of observations was about $\frac{3}{4}$ hour, and during that time the temperature of the room, and hence that of the quartz plate, in no case varied by more than 2° C.

The procedure was in all cases as follows. The room-temperature being steady at about 19° C., the cross wires of the spectroscope were set at a particular wave-length, the iron arc spectrum being used as a standard. Then the reading of the screw head of the quartz plate⁽⁶⁾, necessary to bring into a band coincidence with the cross wires, was observed, *the specimen not yet being in position*. This was repeated for eleven different wave-lengths between 6500 and 4900 Å. Outside this range accuracy of setting was not possible, the bands not being sufficiently well defined.

The specimen was then placed in position in the heater, the temperature of which was raised from that of room-temperature to 28° C. in 1 hour and then maintained constant for a further $\frac{1}{2}$ hour, after which the observations were repeated. From these two sets of observations the values of the residual double refraction n (in wave-lengths) at a temperature of 28° C. were calculated for each of the eleven wave-lengths.

§ 4. EXPERIMENTAL RESULTS AT CONSTANT TEMPERATURE

The values of n are shown in table 1. An attempt was then made to find, if possible, a law of dispersion of n , and it was found that the observations were best fitted by the equation:

$$A, B \qquad \qquad \qquad \frac{n}{\lambda^2} = A - B\lambda \qquad \qquad \qquad \dots\dots(1),$$

λ where A and B are constants for the particular specimen under observation, and λ the wave-length in angstroms.

When the values of n/λ^2 were plotted against λ a very good straight-line graph was obtained in every case, and these graphs are shown in figure 6. The lines do not meet in a point when produced.

n_1 The values of A and B were then calculated for each specimen by the method of least squares, and are shown at the head of the corresponding columns in table 1. From these values of A and B the corresponding values of n were calculated from equation (1), and these are also shown in table 1 in the columns headed n_1 together with the differences $(n - n_1)$. It will be seen from these differences that the agreement between the observed values n and the calculated values n_1 is very good except for the extreme wave-lengths. We may therefore assume that the law of dispersion of the residual double refraction in permanently overstrained celluloid containing 24 per cent of camphor is of the form $n/\lambda^2 = A - B\lambda$.

Next the values of n were plotted against λ for each specimen as shown in figure 7. From these graphs it is seen that for each specimen there is one particular

Table I

λ	Specimen I				Specimen II				Specimen III				Specimen IV			
	$A = 0.629310$ $B = 0.072124$ $\lambda_M = 5816.926$				$A = 0.503809$ $B = 0.057171$ $\lambda_M = 5874.878$				$A = 0.397844$ $B = 0.045983$ $\lambda_M = 5767.987$				$A = 0.297360$ $B = 0.034878$ $\lambda_M = 5683.812$			
	n	n_1	$n - n_1$	n	n_1	$n - n_1$	n	n_1	n	n_1	$n - n_1$	n	n_1	$n - n_1$	n	n_1
6494.993	6.916	6.786	+0.130	5.648	5.589	+0.059	4.279	4.184	4.279	4.184	+0.095	3.069	2.988	+0.081	3.069	2.988
6301.524	6.977	6.941	+0.036	—	5.700	—	4.327	4.292	4.327	4.292	+0.035	3.120	3.080	+0.040	3.120	3.080
6137.702	7.030	7.031	-0.001	5.739	5.760	-0.021	4.358	4.355	4.358	4.355	+0.003	3.143	3.138	+0.005	3.143	3.138
6065.493	7.055	7.058	-0.003	5.748	5.777	-0.029	4.370	4.376	4.370	4.376	-0.006	3.147	3.157	+0.010	3.147	3.157
5895.932	7.067	7.093	-0.027	5.760	5.795	-0.035	4.387	4.405	4.387	4.405	-0.018	3.170	3.188	-0.018	3.170	3.188
5709.395	7.071	7.090	-0.019	5.772	5.782	-0.010	4.390	4.411	4.390	4.411	-0.021	3.186	3.202	-0.016	3.186	3.202
5615.658	7.053	7.073	-0.020	5.764	5.763	+0.001	4.389	4.403	4.389	4.403	-0.014	3.186	3.211	-0.025	3.186	3.211
5506.784	7.044	7.040	+0.004	5.737	5.730	+0.007	4.383	4.386	4.383	4.386	-0.003	3.183	3.193	+0.010	3.183	3.193
5302.315	6.903	6.941	+0.022	5.666	5.641	+0.025	4.342	4.330	4.342	4.330	+0.012	3.166	3.161	+0.005	3.166	3.161
5110.415	6.833	6.809	+0.024	5.553	5.527	+0.026	4.265	4.253	4.265	4.253	+0.012	3.126	3.111	+0.015	3.126	3.111
4903.325	6.613	6.628	-0.015	5.355	5.373	-0.018	4.145	4.144	4.145	4.144	+0.001	3.042	3.038	+0.004	3.042	3.038

λ	Specimen V				Specimen VI				Specimen VII			
	$A=0.193777$ $B=0.023450$ $\lambda_M=5508.941$				$A=0.140091$ $B=0.017424$ $\lambda_M=5360.078$				$A=0.044343$ $B=0.005563$ $\lambda_M=5204.626$			
	n	n_1	$n-n_1$	n	n_1	$n-n_1$	n	n_1	$n-n_1$			
6494.993	1.832	1.749	+0.083	1.215	1.136	+0.079	0.366	0.346	+0.020			
6301.524	1.870	1.827	+0.043	1.247	1.203	+0.044	0.394	0.369	+0.025			
6137.702	1.885	1.878	+0.007	1.258	1.249	+0.009	0.397	0.384	+0.013			
6065.493	1.896	1.896	0	1.267	1.265	+0.002	0.396	0.390	+0.006			
5895.932	1.912	1.930	-0.018	1.281	1.299	-0.018	0.400	0.401	-0.001			
5709.395	1.934	1.952	-0.018	1.301	1.324	-0.023	0.405	0.410	-0.005			
5615.658	1.937	1.958	-0.021	1.314	1.332	-0.018	0.406	0.413	-0.007			
5506.784	1.944	1.960	-0.016	1.318	1.339	-0.021	0.413	0.416	-0.003			
5302.315	1.946	1.952	-0.006	1.335	1.341	-0.006	0.413	0.417	-0.004			
5110.415	1.944	1.931	+0.013	1.343	1.331	+0.010	0.406	0.416	-0.010			
4903.325	1.912	1.894	+0.018	1.336	1.314	+0.022	0.403	0.410	-0.007			

λ_M wave-length λ_M for which n is a maximum. Now from equation (1) this value of λ is given by

$$\lambda_M = 2A/3B.$$

N These values of λ_M for the different specimens are shown at the head of the corresponding columns in table 1. Let us denote by N the particular value which n

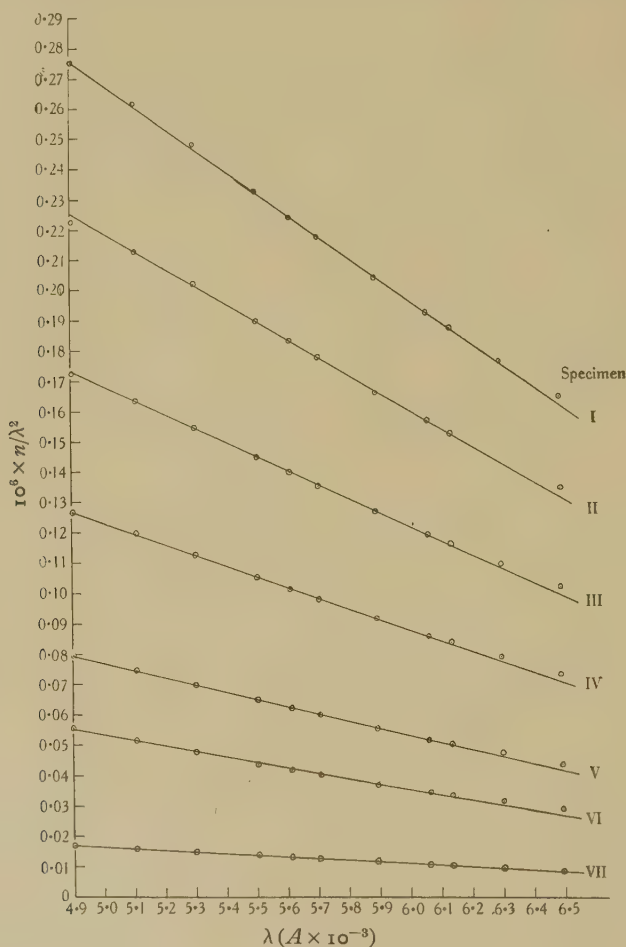


Figure 6.

assumes for $\lambda 5895.932$ in any given specimen. Then as N increases from specimen to specimen λ_M is observed to increase.* Again, from figure 7, for those specimens in which $N > 2$ (i.e. in specimens I-IV) the value of n in the red is greater than that in the blue, but in those specimens in which $N < 2$ (i.e. in specimens V-VII) the value of n in the red is less than that in the blue. On examining the specimens in white light between crossed nicol prisms, it was observed that for those specimens

* There is an exception in the case of specimen I, in which there is a slight decrease.

in which $N > 2$ the natural sequence of colours is reversed in bands above the second order, whilst this second-order band itself is of a dark purple tint and practically achromatic. This reversal in the natural colour-sequence was observed and explained by Savur.

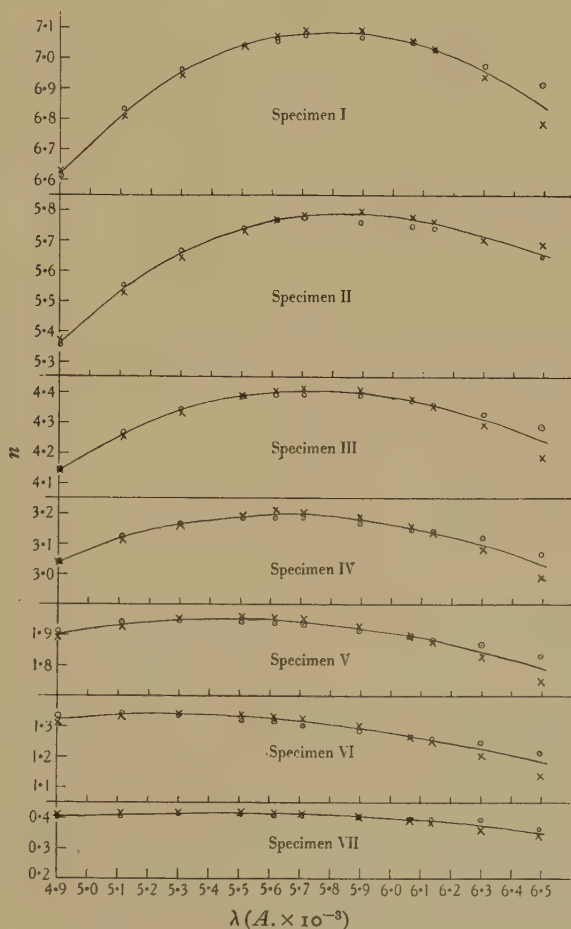


Figure 7.

§ 5. METHOD OF EXPERIMENT AT A SERIES OF TEMPERATURES

The same specimens were used as before, and in each case the following procedure was carried out. After the observations at 28°C. had been made, the temperature of the specimen was slowly raised to 40°C. , the time taken being 1 hour. The temperature was then maintained constant for $\frac{1}{2}$ hour and readings were taken as before, but only for four wave-lengths instead of eleven, so as to avoid keeping the specimen at the higher temperature for too long.

A preliminary set of observations on another specimen had shown that at temperatures less than about 50°C. any time creep in the residual double refraction

was negligible. Above this temperature however the time creep increased rapidly with rise of temperature.

The readings at 40° C. having been taken, the temperature was further raised to 50° C., the time occupied being again 1 hour. The readings were then repeated as before.

§ 6. RESULTS FOR A SERIES OF TEMPERATURES

The values of n as calculated from the observations at 40° C. and 50° C. are shown in table 2, together with the corresponding values at 28° C. When the values of n/λ^2 were plotted against λ , straight lines were again obtained, showing that the same law of dispersion holds at the higher temperatures. The corresponding values of A , B and λ_M also are shown.

The results obtained show that n changes with temperature, and hence it is necessary to extend the definition of N , so that N now denotes the value of n for $\lambda 5895.932$, the specimen being at a temperature of 28° C. It follows from the results given in table 2 that for each of the specimens I–IV, for all of which $N > 2$, the values of n increase as the temperature increases; but in each of specimens VI and VII, for which $N < 2$, the values of n decrease as the temperature increases. In the case of specimen V, for which N is very nearly 2, the change in n with temperature is extremely small.

During the preliminary observations mentioned in § 5 it was found that although for specimens in which N is small there is practically complete recovery (i.e. the values of n regain their former values) when the temperature is again restored to 28° C., this is not the case in specimens in which N is large. In such specimens the effect of heating and cooling is to increase the permanent double refraction.

The results for the seven specimens under observation are shown in figure 8, in which the values of n at $\lambda 5895.932$ for each specimen are plotted against the temperature. From table 2, it is seen that as the temperature increases the values of the constants A and B increase in specimens I–V, in which $N > 2$, but decrease in specimens VI and VII, in which $N < 2$. In specimen V the change is very small.

With regard to the change in the values of λ_M with temperature, it is found that as the temperature increases λ_M decreases for specimens I–V but increases in specimens VI and VII. This change in λ_M is to be expected in view of the change in n with wave-length at the different temperatures. At 28° C. the value of n in specimens I–III is greater in the red ($\lambda 6137.702$) than in the green ($\lambda 5302.315$) but at the higher temperatures, 40° C. and 50° C., the reverse is the case. Owing to observations being made at four wave-lengths only at the higher temperatures, the effect is not well shown in specimens IV and V, although the results tend to show that such is the case. For specimens VI and VII the rise of temperature, although increasing λ_M , does not have such a marked effect on the values of n , which are still less in the red than in the green as was the case at 28° C.

It is quite certain therefore that an appreciable rise of temperature completely changes the character of the dispersion of the residual double refraction, such changes being most marked in specimens for which N is large.

Table 2. Values of the residual double refraction n at different temperatures and different wave-lengths

	Specimen I			Specimen II			Specimen III			Specimen IV		
	28° C.	40° C.	50° C.	28° C.	40° C.	50° C.	28° C.	40° C.	50° C.	28° C.	40° C.	50° C.
A	0.629310	0.621405	0.787973	0.503809	0.593878	0.662430	0.397844	0.452473	0.498440	0.297360	0.337148	0.364428
B	0.072124	0.067710	0.093785	0.057171	0.069995	0.079232	0.045983	0.053473	0.059887	0.034878	0.040838	0.044762
λ_M	5816.926	6118.285	5601.272	5874.878	5656.385	5573.758	5767.987	5641.140	5548.673	5683.812	5503.828	5427.640
n	7.030	7.573	8.049	5.739	6.210	6.675	4.358	4.697	4.969	3.143	3.312	3.447
	7.067	7.627	8.132	5.760	6.283	6.752	4.387	4.754	5.022	3.170	3.349	3.490
	7.053	7.642	8.195	5.764	6.311	6.832	4.389	4.791	5.081	3.186	3.383	3.527
	6.963	7.586	8.207	5.666	6.278	6.836	4.342	4.758	5.110	3.166	3.367	3.554

	Specimen V			Specimen VI			Specimen VII		
	28° C.	40° C.	50° C.	28° C.	40° C.	50° C.	28° C.	40° C.	50° C.
A	0.193777	0.201627	0.203699	0.140091	0.134411	0.125846	0.044343	0.034960	0.035898
B	0.023450	0.024540	0.024777	0.017424	0.016664	0.015500	0.005563	0.004184	0.004392
λ_M	5508.941	5477.506	5480.863	5360.078	5377.300	5525.161	5204.626	5570.427	5448.998
n	1.885	1.933	1.961	1.258	1.229	1.166	0.397	0.354	0.344
	1.912	1.973	1.991	1.281	1.238	1.190	0.400	0.354	0.341
	1.937	1.998	2.020	1.314	1.279	1.217	0.406	0.358	0.355
	1.946	2.020	2.045	1.335	1.304	1.233	0.413	0.362	0.354

Some years ago attempts were made, without much success, to anneal celluloid by slow heating and cooling in water. This process merely had the effect of driving off some of the camphor without decreasing appreciably the residual double

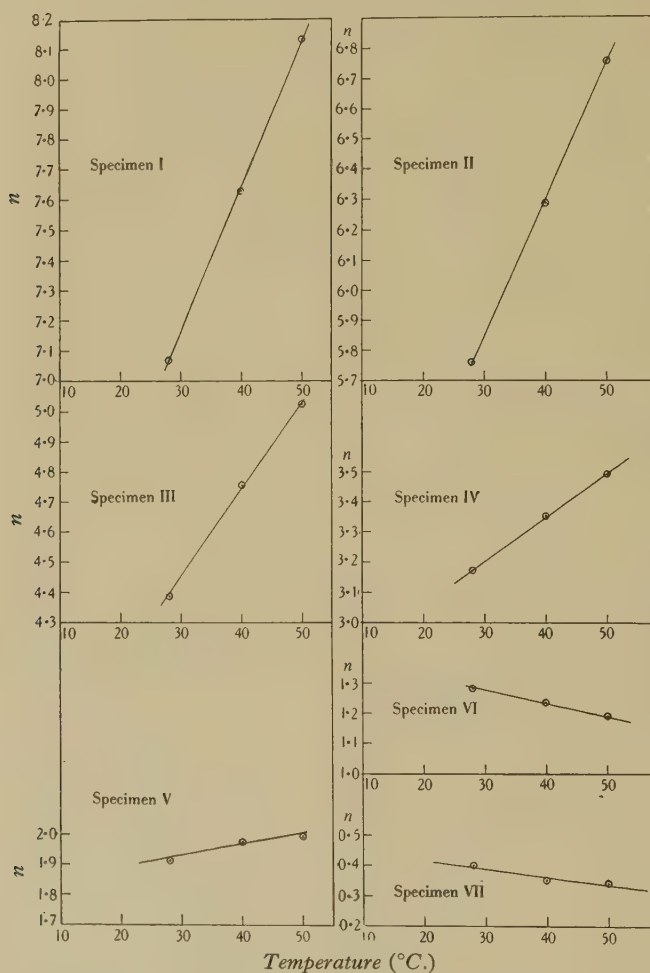


Figure 8. Variation of n with temperature for $\lambda 5895.932$.

refraction N . The reason is apparent from the results here described, and actually for any specimen in which the residual double refraction N is large such a process will tend to increase and not decrease N .

REFERENCES

- (1) SAVUR, S. R. *Proc. roy. Soc. A*, **109**, 338-350 (1925).
- (2) WACHTLER, M. *Z. tech. Phys.* **5**, 418-23 (1924).
- (3) RAMSPECK, A. *Ann. Phys., Lpz., Ser. IV*, **74**, 722-42 (1924).
- (4) DERKSEN, J. C., KATZ, J. R., HESS, KURT, and TROGUS, CARL. *Z. phys. Chem. A*, **149**, 371-81 (1930).
- (5) FILON, L. N. G. and HARRIS, F. C. *Proc. roy. Soc. A*, **130**, 410-31 (1931).
- (6) HARRIS, F. C. *Phil. Mag.* **7**, 80-86 (Jan. 1929).

DISCUSSION

Prof. L. N. G. FILON. One of the results of the paper is of special importance for photoelastic observations, as it shows why efforts to anneal xylonite by heat treatment have been unsuccessful.

Perhaps the authors could give us information on the following points: (1) whether any double refraction introduced by unequal temperature in the windows of the heater enclosing the specimen is likely to have affected the observations; (2) whether the discrepancies between the observed and calculated values of n in the extreme red, which appear to be shown by figures 6 and 7, are significant and could be accounted for by a modification of the formula (1)—for example, by using a formula of the type $n^2 - 1 = \Sigma A_r / (\lambda^2 - \lambda_r^2)$, restricted to a few terms; (3) whether the authors have made any definite observations of the effects of time creep, and, if so, whether the observations show the sense in which this creep operates?

AUTHORS' reply. (1) The glasses used in the windows of the heater were specially selected so as to be free from any initial double refraction. Also they were only attached by soft wax, so that no stress was applied owing to expansion under heat, as might have occurred if they had been enclosed in rigid frames. It is of course always essential to ensure that all lenses, glasses, etc. which are included between the crossed nicols should be free from double refraction. (2) No modification of formula (1) as suggested has been tried as the authors considered the discrepancies between observed and calculated values of n in the extreme red could be accounted for by the comparatively poor visibility in that region. We thank Professor Filon for his suggestion of an alternative formula and will most certainly see if better agreement is obtained by its use. (3) Observations were made at 50° C. on the effects of time creep, with the following results. For specimens in which $N > 2$, the double refraction decreased with lapse of time, but even after five hours it was still very much greater than the original value at 28° C. In those specimens in which $N < 2$, although the double refraction also decreased with lapse of time, its value after only three hours was much less than the original value at 28° C.

A METHOD OF MEASURING SECONDARY-ELECTRON EMISSION FROM FILAMENTS

BY L. R. G. TRELOAR, B.Sc., F.INST.P. A communication from the Research Staff of the M-O Valve Company Limited at the G.E.C. Research Laboratories, Wembley

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ABSTRACT. A method of measuring secondary emission which may have advantages over the usual methods in certain cases is described. The source of electrons is a tungsten filament mounted axially in a cylindrical grid and anode. The filamentary target is placed parallel to the cathode. With the grid connected to the cathode there is a considerable range of positive potentials V_t and V_a on target and anode respectively for which no secondaries can pass through the grid; under these conditions it is shown both theoretically and practically that the target current i_t is proportional to $\sqrt{(V_t/V_a)}$. This law is then used to determine the primary currents for high values of V_a such that all secondaries emitted from the target reach the anode. These, together with the measured values of i_t , give the secondary emission. The possible effects of high velocity secondaries are considered. Application of the method to tungsten and tantalum gives results in agreement with published data.

§ 1. INTRODUCTION

IN the usual method of measuring secondary emission, which has been described by Petry⁽¹⁾ among others, a narrow beam of electrons is allowed to fall on a plate of the material whose secondary emission is to be investigated, this plate or target being surrounded by a collecting-chamber maintained at a suitable positive potential with respect to it. The target must be of such a size that one can be sure that all the electrons in the beam will strike it; then by measuring the currents to the target and to the collector the secondary emission of the target may be obtained. This method does not lend itself readily to the study of the effect on secondary emission of surface contaminations of atomic thickness, for instance of electro-positive metals, since the heat treatment of the target necessitates the dissipation of a considerable quantity of energy in the tube, and this is liable to give rise to undesired contamination owing to evolution of gas from the surrounding electrodes or glass envelope. Doubtless this disadvantage could be overcome by means of appropriate modifications, but it would nevertheless be much simpler, from the practical point of view, if a method could be found of using materials in the form of filaments for the measurement of secondary emission, since a filament may readily be raised to a high temperature without any considerable heating occurring in other parts of the tube.

Since it is not possible to produce an electron beam whose thickness would be less than the diameter of a filament, it is necessary to immerse the filament com-

pletely in a stream of electrons and to determine how many electrons will strike it under given conditions. It is the purpose of this paper to show that it is possible, by using a suitable arrangement of electrodes, to determine the magnitude of the electron current to such a filament and the way in which it varies with the relative potentials of the filament and the other electrodes.

§ 2. THE PRINCIPLE OF THE METHOD

The arrangement of electrodes used in this method is shown in figure 1. *A* is a cylindrical anode, *G* a concentric grid close to the anode, and *C* a thermionic cathode. The filament *T* (referred to subsequently as the target) whose secondary emission is to be studied is stretched parallel to *C* and at a distance from it of about half the radius of the grid.

If now the grid is maintained at zero potential, potentials being referred to the cathode, and a potential V_t is applied to the target whilst the anode potential V_a is varied, there will be, for a considerable range of V_a , a potential-minimum between *T* and *A* which will effectively prevent the passage of secondary electrons either from *T* to *A* or from *A* to *T*, according to whether $V_t <$ or $> V_a$. It is assumed

V_t, V_a

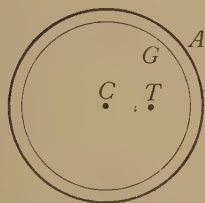


Figure 1. Illustrating the principle of the method.

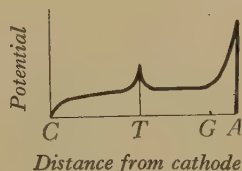


Figure 2(a).

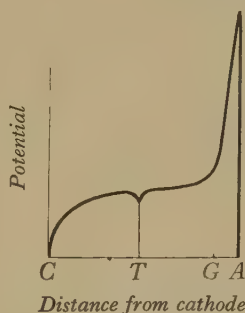


Figure 2(b).

Diagrammatic representation of space potentials.

for the present that all the secondaries are emitted with zero velocity; the validity of this assumption will be examined later. It is also assumed that the space charge due to the electrons is negligibly small. The condition in which there is a potential minimum between *T* and *A* is represented diagrammatically in figure 2 (a), which gives the approximate potential-distribution along a straight line from the cathode through the target and through a space between the grid wires to the anode.

But if the anode potential be sufficiently high the potential-minimum will no longer exist (figure 2 (b)). At any point within the grid and not very close to it the combined field due to the anode at potential V_a and the grid at zero potential is approximately equivalent to that which would be produced by an anode at a potential $V_a/(m+1)$ placed approximately at the position occupied by the grid, m being the amplification factor of the grid-anode system. Hence when the anode potential is somewhat higher than $(m+1) V_t$ all the secondaries from the target will pass through the grid to the anode.

m

Thus by the use of appropriate anode potentials we can either prevent any of the secondaries from the target from reaching the anode, or cause all of them to reach it, and in neither case will secondaries from the anode reach the target. If now we can find a law relating the current that flows to the target with anode voltage over the region in which secondary emission is absent, we may use this law to calculate the primary current I_p incident on the target in the region in which secondary emission current I_s is present. The current actually measured in the latter case will be $(I_p - I_s)$. Hence we shall be able to determine I_p and I_s .

§ 3. THE RELATION BETWEEN TARGET CURRENT AND ANODE VOLTAGE

Let us imagine the grid to be absent, and let the target filament be assumed to be so small that its field may be considered to be negligible at a distance from it which is small compared with the radius of the anode. The radial flow of the electrons approaching the target in these circumstances may be represented approximately by a flow along parallel straight lines with uniform velocity v (figure 3). The electrons near the target will be deflected into curved orbits, and the current to the target will be proportional to the distance d from the central undeviated orbit to the undeviated portion of the orbit tangential to the target. This distance may be calculated by making use of the fact that the angular momentum of a particle in a central orbit is constant. If v' is the velocity of the particle at the point of contact with the target, we have therefore

$$a \quad mvd = mv'a,$$

$$\text{or} \quad d = v'a/v,$$

where a is the radius of the target. Converting the velocities into potentials, and remembering that the current i_t to the target is $2\rho dl$, where ρ is the current-density of the approaching electrons and l is the length of the filament, we obtain

$$i_t = 2\rho al \sqrt{(V_t/cV_a)} \quad \dots\dots(1a),$$

where c is the constant ratio which the space potential in the neighbourhood of T due to the anode bears to the potential of the anode. The presence of a grid at zero potential will change the constant c to c' , where

$$(m+1)c' = c,$$

and the current is then given by

$$i_t = 2\rho al \sqrt{\left(\frac{m+1}{c} \cdot \frac{V_t}{V_a}\right)} \quad \dots\dots(1b).$$

Thus, in all cases we have $i_t \propto \sqrt{(V_t/V_a)}$.

If we maintain a constant potential on the target and vary the anode potential, the grid being at zero potential, the curve relating target current with $\sqrt{(V_t/V_a)}$ will fall into three parts, which are represented in figure 4. For low values of V_a there will be no secondary electrons passing through the grid. The curve should, therefore, correspond with the theoretical straight line through the origin— AB in figure 4.

This portion of the curve should be the same for all values of V_t . At sufficiently high values of V_a all the secondaries will reach the anode. In this region the primary current will still be represented by the continuation of AB , but the actual current

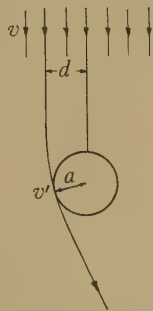


Figure 3. Electron orbits near charged wire.

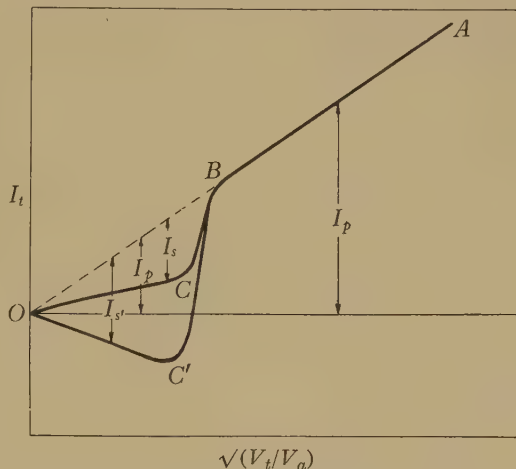


Figure 4. Diagram illustrating the method of obtaining I_p and I_s .

$(I_p - I_s)$ will be another straight line through the origin, since I_s/I_p is constant if V_t is constant. For different values of V_t different lines OC , OC' , ... will be obtained. The intermediate portion BC of the curve represents the condition where some but not all of the emitted electrons leave the target. This portion is of no interest for the purpose of measurement.

§ 4. THE PREPARATION OF THE TUBE

We come now to the practical details of the method. A longitudinal section of the electrode system is shown in figure 5. The anode A was a nickel cylinder 40 mm. long and 25 mm. in diameter. The grid G , of diameter 22 mm., was wound with 0.11-mm. molybdenum wire to a pitch of 2.1 mm. on two 0.6-mm. nickel supporting wires. The cathode C was a 0.105-mm. tungsten wire 12 mm. long supported by 0.6-mm. nickel leads. The purpose of making it short was to reduce the effect of irregularities in the field in the neighbourhood of the ends of the electrodes. The target T was, in the first instance, a tungsten filament of diameter 0.105 mm. Both filaments were maintained in tension by springs mounted on wires N and N' attached at the base to the pinch L and at their other ends to the hard glass bead B' which, together with a similar bead B , provided the necessary support for the electrode system. It was found necessary to provide end plates D , D' , connected to the grid, having 3-mm. holes for the passage of the wires, to prevent undesirable effects due to charges on the glass bulb. A nickel disc carried a getter pellet H of copper-clad metallic barium which when heated by induction caused a barium deposit to form on the bulb for the purpose of removing residual

gas from the tube. The whole system was sealed into a bulb about 130 mm. long and 40 mm. in diameter.

The tube was pumped with a mercury diffusion pump. After being baked for 10 minutes at 400° C. the electrodes were heated by induction to redness for a few minutes and the getter was dispersed on to the bulb. The tube was then sealed off.

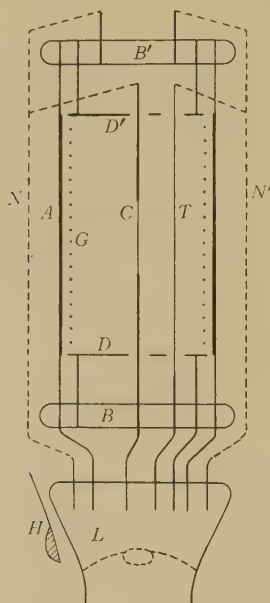


Figure 5. The tube.

§ 5. THE MEASUREMENT OF THE PRIMARY CURRENT

In using the tube it was necessary to avoid space-charge effects. The cathode was, therefore, operated at such a temperature that its emission was saturated. Normally the anode, or anode plus grid, current was maintained in this way at 1.0 mA., and since the fraction of the current arriving at the target was never more than about 1 per cent, this value of anode current was taken to be equal to the total emission from the cathode:

V_g When the grid voltage V_g was zero and V_t was constant, the variation of the target current i_t with anode voltage was measured. The relation between i_t and $\sqrt{(V_t/V_a)}$ for a number of target voltages is shown in figure 6. It is at once evident that the form of the relation given by equation (1b) is satisfied, the points lying roughly on a straight line passing through the origin. The line calculated from the dimensions of the electrodes by means of equation (1b) is shown dotted. The fact that the measured currents are 16 per cent higher than the calculated values is probably due to the non-fulfilment of the condition, used in deriving the equation, that the effective field of the target extends over only a very small area. However,

the difference in the numerical constant does not affect the accuracy of the experiments, provided that the relation $i_t \propto V_t/V_a$ is satisfied.

It will be seen that a departure from linearity occurs at about $\sqrt{(V_t/V_a)} = 0.6$. At this point the anode voltage becomes sufficiently high to draw some of the secondaries through the grid. But we may safely assume that at this and lower values of $\sqrt{(V_t/V_a)}$ the primary current is given accurately by the straight line through the origin.

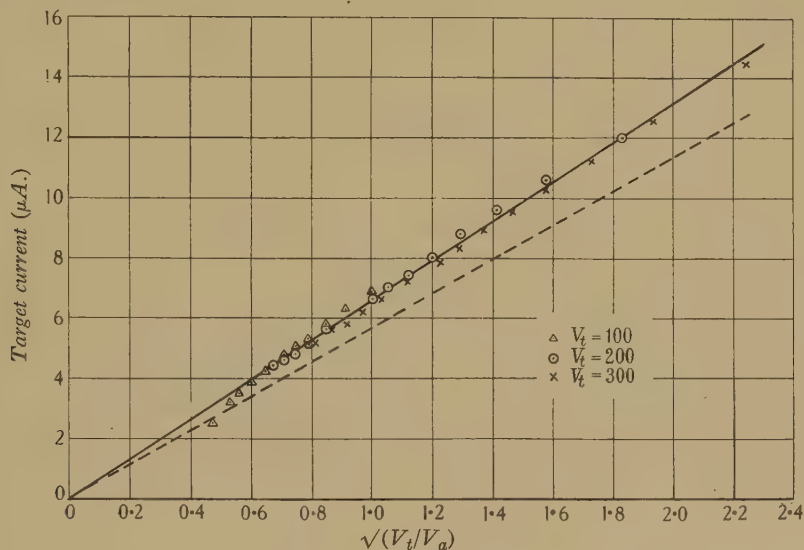


Figure 6. Primary current as a function of electrode voltages.

§ 6. THE MEASUREMENT OF THE SECONDARY CURRENT

In figure 7 the calibrating line for the primary current C obtained in the manner just described is plotted with $\sqrt{\{(m+1) V_t/V_a\}}$ as abscissa. Curve B shows the measured values of i_t , when $V_t = 50$ V., also plotted against $\sqrt{\{(m+1) V_t/V_a\}}$. The difference between corresponding ordinates of curves C and B gives a measure of the secondary current leaving the target at each value of abscissa. It will be seen that from abscissa 1.0 downwards the points on curve B fall very close to another straight line D through the origin. In this region the field is such that all the secondaries emitted from the target are attracted towards the anode; the secondary current is therefore proportional to the primary current, as it should be, and the ratio of the slopes of the straight lines D and C is $(I_p - I_s)/I_p$, from which the secondary-emission coefficient I_s/I_p may be obtained.

At a target voltage of 300 it would be necessary to apply about 1200 V. to the anode in order to draw all the secondaries through the grid. If, however, the grid is connected to the anode about 400 V. is sufficient. A voltage V_{ga} on grid and anode may be converted into a voltage V_a on the anode and 0 on the grid by the relation $V_a = (m+1) V_{ga}$.

This method has been verified by the results given in figure 7. Curve *A* shows the target current, taken with the anode and grid connected, when $V_t = 50$ V. Current is plotted against $\sqrt{(V_t/V_a)}$ instead of $\sqrt{\{(m+1)V_t/V_a\}}$, which was used as abscissa for curve *B*. Hence for a given value of abscissa the potential con-

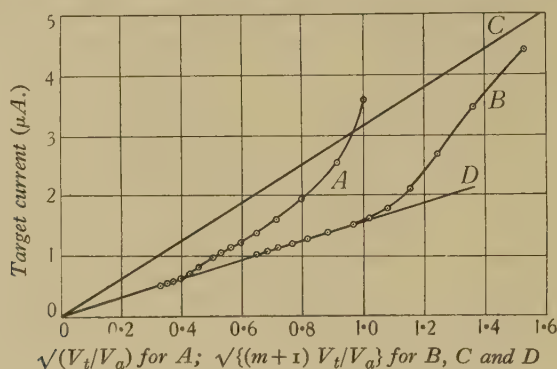


Figure 7. Total current as a function of electrode voltages. $V_t = 50$; $V_g = V_a$ for *A* and \circ for *B*.

ditions within the grid are identical in each of the cases represented by curves *A* and *B*. The line *C*, therefore, represents the primary current for *A* as well as for *B*. Differences between the two curves are due to differences in the amount of secondary emission passing between target and anode. But when all the secondaries emitted

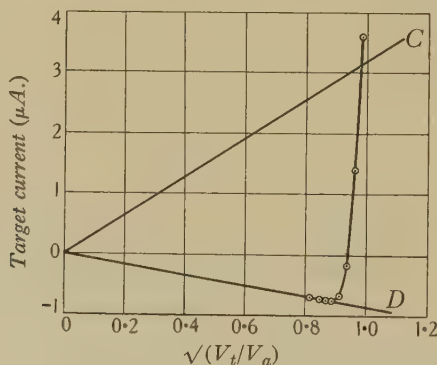


Figure 8. Total current as a function of electrode voltages. $V_t = 300$.

by the target reach the anode and none of the anode secondaries reach the target, the curve *A* approximates to a straight line through the origin. The fact that the same line also represents the saturated secondary emission in the case of curve *B* is a proof of the equivalence of the two methods of measurement.

The curve of secondary emission taken when $V_t = 300$ V. and $V_a = V_g$ is given in figure 8. In this case saturation is obtained when V_a is about 400 V. The negative slope of *D* represents a ratio I_s/I_p greater than unity.

§ 7. APPLICATION OF METHOD TO TUNGSTEN AND TANTALUM

The variation of the secondary-emission coefficient with the voltage of the primary electrons for the case of a tungsten filament (previously heated at about

2800° K. for a few minutes) is shown in figure 9 by the continuous line. For comparison the results obtained by Petry⁽²⁾ and Krefft⁽³⁾ by means of the method referred to in § 1 are also given. The differences between the three curves are no greater than would be expected to arise from slight differences in the material or in the state of contamination of its surface.

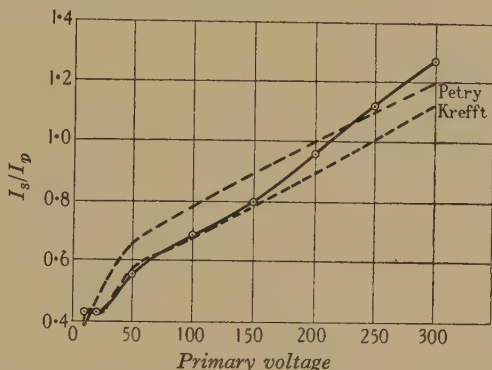


Figure 9. Secondary-emission coefficient for tungsten.

A similar curve, figure 10, for tantalum is in good agreement with the result obtained by Warnecke⁽⁴⁾, by a method similar to that used by Petry.

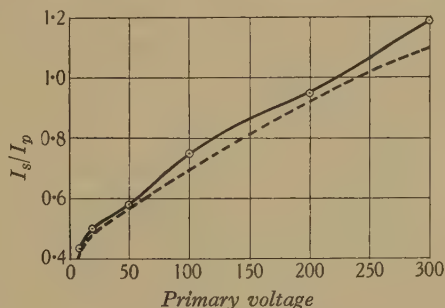


Figure 10. Secondary-emission coefficient for tantalum — author's results; ——— Warnecke's results.

§ 8. THE EFFECT OF HIGH-VELOCITY SECONDARIES

In considering the method of obtaining the calibrating line for the primary current, we assumed that all secondaries, either from the anode or from the target, were emitted with zero velocity. We must now consider the effect of finite velocities of emission. If the secondaries all had a velocity low in relation to that of the primaries a straight line would still be obtained, although its range would be somewhat diminished. If, however, the secondaries had a range of velocities extending up to the primary velocity, these secondaries would begin to pass through the grid at different values of the abscissae, and a departure from linearity would result. If, however (and this is more nearly what happens) there were a number of low-velocity secondaries, which have no important effect, and also a number having very nearly the full primary velocity, these latter would always pass through the

grid. We must consider separately the secondaries leaving and arriving at the target. The number of those leaving the target would be proportional to the primary current. Such emission would reduce the slope of the line obtained when i_t is plotted against $\sqrt{(V_t/V_a)}$, but would not cause a departure from linearity. Straight lines corresponding to different values of V_t would, however, no longer be coincident, unless the proportion of such high-velocity secondaries were independent of primary voltage.

Of the secondaries leaving the anode, most will traverse the space within the grid and strike the anode again, but there will be a fraction which strike the target. The fraction thus collected by the target will decrease with increasing anode voltage, and it is possible that this fraction might be proportional to $\sqrt{(V_t/V_a)}$. But only in the case where the amount of high-velocity secondary emission is independent of primary voltage will a series of coincident straight lines be obtained for different values of V_t . Hence it is possible to obtain a straight line independent of V_t only if there is a high-velocity fraction of the secondaries which is independent of the primary voltage.

Let us now examine the experimental evidence with regard to high-velocity emission. Farnsworth⁽⁵⁾ has found that for the metals nickel, copper, iron and silver, the full-velocity secondary emission, measured relatively to the primary current, ranges from 11 to 28 per cent at 10 V. and from 5 to 10 per cent at 50 V., while Haworth⁽⁶⁾ found in the case of molybdenum that this ratio continues to fall from 50 to 125 V., being only 4 per cent of the total secondary emission (and therefore also about 4 per cent of the primary current) at the latter voltage. Hence the high-velocity secondary emission is not independent of voltage, and its effect should, therefore, be apparent in the curvature and non-coincidence of the calibrating lines taken with different target voltages. At the values of target voltage (100 to 300) used in the present work the errors would probably be from 2 to 4 per cent. The calibrating lines actually obtained are neither perfectly straight nor perfectly coincident, but the experimental errors of the readings are probably about 3 per cent, so that we cannot be sure that these irregularities are due to high-velocity emission. We may say that, to the degree of accuracy attained by the experiments, the effects of the initial velocities of the secondary electrons may be neglected.

§ 9. ACKNOWLEDGMENT

The author desires to tender his acknowledgment to the Marconiphone Company and the General Electric Company on whose behalf the work which has led to this publication was done.

REFERENCES

- (1) PETRY, R. L. *Phys. Rev.* **26**, 346 (1925).
- (2) ——— *Phys. Rev.* **28**, 362 (1926).
- (3) KREFFT, H. E. *Phys. Rev.* **31**, 199 (1928).
- (4) WARNECKE, R. *J. Phys. Radium*, **5**, 267 (1934).
- (5) FARNSWORTH, H. E. *Phys. Rev.* **31**, 405 (1928).
- (6) HAWORTH, L. J. *Phys. Rev.* **48**, 88 (1935).

DISCUSSION

D. O. SPROULE. It is clear that in this method the electrons are incident on the filament at all possible angles. Hence the question of dependence of secondary emission on angle of incidence may be important. I recall having seen a report of an investigation of this factor, but do not remember the nature of the results. Could the author throw some light on this aspect of the problem, at least so far as it is relevant to this method?

Dr A. L. REIMANN. In considering the possible effects of the varying angles of incidence of the primary electrons on the results obtained by Mr Treloar, I think it should be borne in mind that, owing to the multicrystalline microstructure exhibited by the surfaces of heat-treated metals, the range of angles of incidence with crystal faces must be just as great in any experiment where a definite parallel beam of electrons is directed at any angle on to a macroscopically plane surface of a multicrystalline specimen. In the case of such specimens, no important variation of secondary emission phenomena with apparent angle of incidence is to be expected.

AUTHOR'S reply. If the amount of secondary emission is dependent on the angle of incidence of the primary electrons, this factor will have to be taken into account in making use of this method of measurement. I have not been able to find any direct experimental evidence on this point for the case of multi-crystalline surfaces bombarded with slow electrons. It seems certain, however, that the primary electrons will be scattered through large angles by the metallic nuclei before losing most of their energy, so that any effect of their original direction is not likely to be very marked.

THE THERMAL CONSTANTS OF SETTING CONCRETE

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ABSTRACT. The rise in temperature in a large mass of concrete during setting may be considerable, and the shrinkage stresses induced by the subsequent cooling may become large enough to cause cracking. It is, therefore, important to be able to calculate the rise of temperature likely to occur in such a mass. The calculation of the temperature-rise requires a knowledge of the thermal constants of the material. Hitherto no measurements have been made on concrete less than three days old, and the experiments made have mostly been on dry concrete. The values of the constants so obtained may differ considerably from those for fresh concrete. Methods have therefore been developed whereby measurements of the thermal conductivity and the thermal diffusivity of setting concrete can be made.

The thermal conductivity has been obtained by measuring the heat-flow between coaxial cylinders, and the diffusivity has been measured by means of observations on the rapid cooling of a cylindrical specimen. In both cases the effects of the heat evolved by the concrete have been eliminated by making experiments in a water bath controlled so that its rate of rise of temperature is the same as that produced in the concrete by the latter's own heat-evolution.

The accuracy of the methods has been tested by means of experiments on water. Good agreement is obtained with the results of Martin and Lang, which are probably the most reliable of previous data for water. Results are quoted for typical concrete specimens, and the values of the conductivity and the diffusivity obtained are compared with those for dry concrete.

§ 1. INTRODUCTION

IN the designing of concrete structures it is frequently of importance to be able to estimate the temperature-rise which will be produced in a given mass of concrete by the heat evolved during setting. For this to be computed it is essential to know the size and shape of the mass and the nature of its surroundings, the thermal constants of the concrete, and its rate of evolution of heat at any time.

The methods of calculating from these data the temperature-rise for masses of concrete of various simple geometrical forms have been fully discussed by Fox^(1, 2) and by Davey and Fox⁽³⁾. The mean values of the conductivity and diffusivity recommended by Davey and Fox are, however, open to some objection in that they are deduced from a consideration of experimental results on dry concrete at least three days old. It is known that the amount of moisture present in concrete has a considerable effect on the thermal conductivity, and since concrete during setting

is usually almost completely saturated with water, it might be expected to have a considerably higher conductivity than dry concrete. Furthermore, during the setting period some of the water combines with the cement, and the resulting decrease in the amount of free water present is likely to affect the values of the thermal conductivity and diffusivity of the concrete.

The object of the work described here has been to investigate these changes and to obtain more reliable mean values of the thermal constants of setting concrete for use in calculations of temperature-rise. Furthermore, a method has been developed at the Building Research Station for measuring the temperature-rise of concrete while this is setting under adiabatic conditions, and in order that the heat evolved may be calculated from this temperature-rise an accurate knowledge of the specific heat of the material is required.

Since the rate of the chemical reaction is affected appreciably by the temperature of the material, it is important to specify accurately the conditions of storage of the specimens during the setting period. Two simple methods of storage suggest themselves: (*a*) at constant temperature, and (*b*) under adiabatic conditions. In practice, more particularly in large masses of concrete, the conditions more nearly approximate to (*b*) than to (*a*). A further advantage of adiabatic storage is that it enables the effects of the heat evolved by the concrete to be eliminated easily from the experimental results. This method of storage has therefore been adopted.

The method of securing adiabatic conditions of storage for concrete specimens during setting has been fully described by Davey⁽⁴⁾ and is only outlined briefly here. A specimen having the same constitution, and mixed at the same time as those to be studied, is enclosed in a vacuum flask which is immersed in a water bath. A thermocouple with one junction in the control specimen and the other in a glass tube immersed in the bath is connected to a sensitive relay system, which switches the immersion heaters in the bath on or off according as the temperature of the water is below or above that of the control specimen. Thus the temperature of the water never differs appreciably from that of the concrete, which is thereby prevented from exchanging heat with its surroundings. The accuracy with which the temperatures of the bath and the specimen can be made to agree depends on the sensitivity of the relay system. With the system used in the present work the two temperatures agreed at all times within $\frac{1}{10}^{\circ}$ C. The test specimens were stored in a bath controlled in this way, and by taking the temperature of the bath as the datum for all temperature measurements, the effects of the heat-evolution of the concrete were eliminated. Since the thermal constants are likely to be changing with time, small specimens were used so as to reduce the duration of the individual measurements.

The thermal conductivity k , and the thermal diffusivity h^2 , were chosen for measurement as being most convenient. From these two quantities and the density ρ the specific heat s can be calculated if required, by means of the formula

$$s = k/h^2\rho.$$

The methods of determining k and h^2 will be described separately.

§ 2. MEASUREMENT OF THERMAL CONDUCTIVITY

The thermal-conductivity measurements were made by the well-known method depending on the heat-flow between coaxial cylinders.

The specimens were cast in the annular space between two coaxial brass tubes *A* and *B*, figure 1, 20 cm. long and of radii 2.13 and 0.40 cm. respectively. The ends of the tube *A* were closed by rubber bungs in which holes were bored centrally to carry the tube *B*. A 40 s.w.g. constantan wire stretched down the centre of tube *B*.

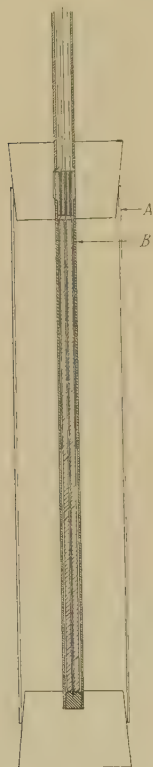


Figure 1. Longitudinal section of conductivity specimen.

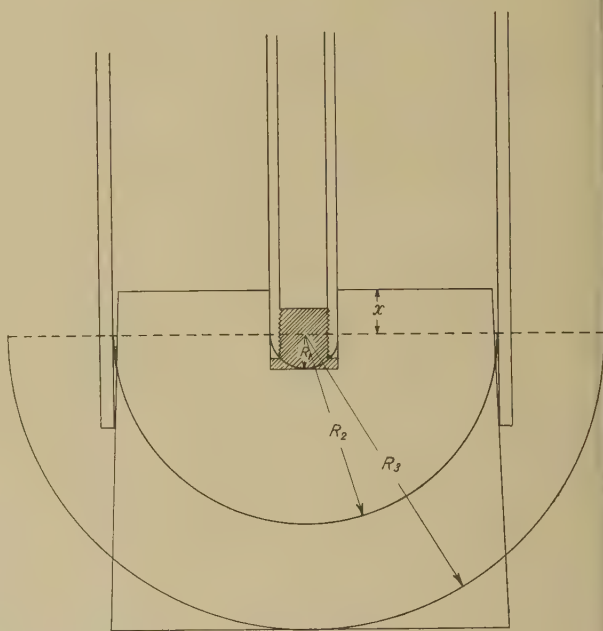


Figure 2.

formed the heating element. It was soldered at one end to a small brass plug which screwed into the bottom of the tube *B*. The other end of the heater wire was soldered to a 40 s.w.g. copper wire which passed out through a small hole in an ebonite plug at the upper end of the tube. The wires were silk-covered, and were further insulated by a coating of cellulose paint. A glass capillary tube which just fitted inside the inner brass tube surrounded the heater wire, the spaces between the glass and the wire and between the glass and the brass tube being filled with oil. In this way good thermal contact between the wire and the tube was secured, together with good electrical insulation. Another 40 s.w.g. copper wire was soldered to the upper end of tube *B* to provide the return lead for the current.

The temperature-difference between the two brass tubes was determined by means of 40 s.w.g. copper-constantan thermocouples soldered to the tubes. The wires forming the inner thermocouple passed down the inside of the tube *B*, and were soldered into small holes drilled diametrically opposite each other in the wall of the tube. These wires were insulated in the same way as the heater wire before they were soldered into position inside the tube. The outer thermocouple was soldered on to the outside of the tube *A*, the wires being protected from the water by several coats of cellulose paint. Owing to a large e.m.f., presumably of electrolytic origin, which was always present when the space between the tubes was filled with concrete, it was not possible to determine the temperature-difference directly by a single differential thermocouple. The two thermocouples accordingly had separate cold junctions which were placed in small glass tubes filled with paraffin and immersed in the water bath.

The e.m.fs. of the two thermocouples were read on a Tinsley thermocouple potentiometer. This instrument was calibrated directly in microvolts, and by observing galvanometer deflections readings could be made with an accuracy of a quarter of a microvolt. Since the difference between the two required e.m.fs. was of the order of 120 μ V. it could be measured with an accuracy of 1 part in 400. The corresponding temperature-differences were read from a large-scale graph obtained with the aid of Beckmann thermometers. A current of about 0.8 A., supplied from a 12-volt battery, was passed through the heater wire, and maintained in the steady state a temperature-difference of about 3° C. between the two brass tubes.

With specimens of the dimensions given above, the steady state was reached in about 10 minutes after the switching on of the current. This steady state was, of course, only a steady state with respect to the controlled bath. Actually the whole specimen was rising in temperature at the same rate as the bath, but the heat required to maintain this rise was supplied by the concrete itself. Thus all the heat supplied to the heater, with the exception of certain small corrections to be discussed later, flowed out radially through the specimen, and the usual equation for heat-flow between coaxial cylinders could be applied, namely,

$$Q = 2\pi k (\theta_1 - \theta_2) / (\log_e R_2 - \log_e R_1) \quad \dots\dots(1),$$

where Q is the radial heat-flow per unit length per second, θ_1, θ_2 are the temperatures of the inner and outer cylinders respectively, R_1, R_2 are the radii of the cylinders, and k is the thermal conductivity of the material.

The quantity of heat measured was the total quantity Q_0 supplied to the heater per second. Since the inner brass tube had a wall-thickness of about 0.1 cm., and must therefore have been practically at uniform temperature throughout its length, we can assume that the radial flow of heat was uniform over the whole length of the specimen.

$$\text{Thus} \quad Q \times l = Q_0 - 2H (\theta_1 - \theta_2) - C \frac{d\theta_0}{d\tau} \quad \dots\dots(2),$$

where l is the length of the specimen, H is the heat-loss from one end of the specimen for unit difference of temperature between the inner and outer cylinders, C is the

Q, θ_1, θ_2
 R_1, R_2
 k
 Q_0

l, H
 C

θ_0, τ heat capacity of the inner brass tube and its contents, and $d\theta_0/d\tau$ is the rate of rise of temperature of the controlled bath during the experiment.

The quantity H cannot be calculated exactly owing to the shape of the rubber bungs closing the ends of the tube. Being small, however, compared with Q_0 , it can be estimated with sufficient accuracy by the method adopted below.

x
 R_3 A longitudinal section of the lower end of the specimen is shown in figure 2. The heat-loss through the bung may be regarded as made up of two parts: (1) the loss between concentric cylinders of radii R_1 and R_2 and length x , and (2) the loss between concentric hemispheres of radii R_1 and R_2 , or R_1 and R_3 . If we take R_1 and R_2 for the radii of the hemispheres, the loss obtained will certainly be greater than that actually occurring, while if we take R_1 and R_3 , the calculated loss will probably be too small. The two values thus obtained do not differ very widely, and their mean may be taken as sufficiently accurate for our purpose.

The values of R_1 , R_2 and R_3 were respectively 0.40, 2.13, and 2.50 cm., while x measured 0.6 cm. Taking k for rubber as 0.45×10^{-3} , we thus obtain for the cylindrical loss

$$H = 2\pi kx / (\log_e R_2 - \log_e R_1) \\ = 0.0008 \text{ cal. per sec. per } ^\circ\text{C. temperature-difference,}$$

and for the hemispherical loss

$$H_s < 2\pi k R_1 R_2 / (R_2 - R_1) \\ < 0.0014 \text{ cal. per sec. per } ^\circ\text{C. temperature-difference,}$$

and

$$H_s > 2\pi k R_1 R_3 / (R_3 - R_1) \\ > 0.0013 \text{ cal. per sec. per } ^\circ\text{C. temperature-difference.}$$

Thus H lies between 0.0022 and 0.0021 cal. per sec. per $^\circ\text{C.}$ temperature-difference between the tubes, or, taking the mean value,

$$H = 0.00215 \text{ cal. per sec. per } ^\circ\text{C.}$$

Assuming a similar loss at the upper end of the specimen, we have finally

$$2H = 0.0043 \text{ cal. per sec. per } ^\circ\text{C.}$$

The total heat-input, Q_0 , necessary to maintain a temperature-difference of 3°C. between the tubes was of the order of 1.3 cal. per sec., so that the heat-loss from the ends is only about 1 per cent of the total input. The error involved by using the above approximate calculation of end losses will thus be negligible.

C The third term on the right of equation (2) represents the heat required to produce in the inner brass tube and its contents a temperature-rise exactly similar to that of the controlled bath. The thermal capacity C of the tube and its contents could be calculated from the specific heats and masses of the separate constituents and was approximately equal to 2 cal. per $^\circ\text{C.}$ Since the rate of rise of temperature of the bath never exceeded 2°C. per hour during an experiment, and was usually less than 1°C. per hour, this term cannot account for more than one-tenth of 1 per cent of the total heat-input, and it has accordingly been neglected.

A further small error may arise from the fact that the rate of heat-evolution of the concrete depends on its temperature. During an experiment the centre of the

conductivity specimen is raised in temperature above the controlled bath, and will thus be evolving heat more rapidly than when the specimen is unheated. Thus more heat will be produced by the concrete than is necessary to maintain the correct rate of rise of temperature in the specimen, and the excess heat will be added to the radial flow. But since the temperature-excess at the centre is only about 3°C. , and since, moreover, owing to the logarithmic decrease of temperature with radius, only a very small part of the concrete is seriously affected, this error may also be neglected.

The possibility of error in the thermal-conductivity experiments due to the two cylinders not being accurately coaxial is discussed in the Appendix, where it is shown that the error from this cause is not likely to exceed one-half of 1 per cent. The thermal-conductivity measurements will therefore be in error by an amount not exceeding 1 per cent.

§ 3. MEASUREMENT OF THERMAL DIFFUSIVITY

Consider a cylinder of radius R supposed infinite in length, and having an initial temperature-distribution given by

$$\theta = f(r). \quad R, \theta, f, r$$

Suppose that the cylinder is placed, at time τ equal to 0, in surroundings at zero temperature, and that the rate of heat-loss from the surface is proportional to the difference of temperature between the surface and the surroundings.

The equation of heat-flow in the cylinder is

$$\frac{\partial \theta}{\partial \tau} = h^2 \left(\frac{\partial^2 \theta}{\partial r^2} + \frac{1}{r} \frac{\partial \theta}{\partial r} \right) \quad \dots\dots(3), \quad h$$

and the boundary conditions to be satisfied are

$$\theta = f(r) \quad \text{at} \quad \tau = 0 \quad \dots\dots(4)$$

and

$$-k \frac{\partial \theta}{\partial r} = E\theta \quad \text{at} \quad r = R \quad \dots\dots(5),$$

where E is the amount of heat lost per cm^2 per sec. from the surface for unit difference of temperature between the surface and the surroundings.

It can then be shown⁽⁵⁾ that the temperature at any point in the cylinder at time τ is given by the equation

$$\theta = \sum_1^{\infty} A_n J_0(\alpha_n r) e^{-\alpha_n^2 h^2 \tau} \quad \dots\dots(6),$$

where A_n, α_n are constants.

But the values of $\alpha_1, \alpha_2, \dots$ form an increasing series, and thus for large values of τ the higher terms of the series represented by equation (6) will be small compared with the first. Thus for sufficiently large values of τ we can neglect all terms except the first and the solution becomes

$$\theta = A_1 J_0(\alpha_1 r) e^{-\alpha_1^2 h^2 \tau}.$$

For concrete specimens of the dimensions used in the present tests, this simplification was permissible at values of τ greater than 120 sec. Hence if θ_1

is the temperature at some point inside the cylinder at time τ_1 , and θ_2 is the temperature at the same point at a later time τ_2 , we have

$$\frac{\theta_1}{\theta_2} = e^{-\alpha_1^2 h^2 (\tau_1 - \tau_2)},$$

i.e.
$$h^2 = (\log_e \theta_1 - \log_e \theta_2) / \alpha_1^2 (\tau_2 - \tau_1) \quad \dots\dots(7).$$

θ_0, θ_R Also, if θ_0 and θ_R are the temperatures at the axis and surface of the cylinder respectively at the same time, we have

$$\theta_0 / \theta_R = J_0(0) / J_0(\alpha_1 R) = 1 / J_0(\alpha_1 R),$$

i.e.
$$J_0(\alpha_1 R) = \theta_R / \theta_0 \quad \dots\dots(8).$$

Since equations (7) and (8) involve only ratios of temperatures, it is sufficient to measure quantities which are proportional to temperatures. Equation (8) then serves to determine α_1 , and h^2 can be calculated from equation (7).

Experimental procedure. The measurements of diffusivity were made with specimens identical with those used for the conductivity determinations, except that they had a single copper-constantan thermojunction of 40 s.w.g. wire at the centre instead of the inner brass tube.

The specimen was kept in the controlled bath until a measurement of the diffusivity was to be made, when it was removed and placed for a few minutes in a bath at a temperature about 10° C. lower than that of the controlled bath. During this period, if it be assumed that the cooling was entirely radial, the specimen acquired a temperature-distribution of the form $\theta = f(r)$.

The specimen was then quickly replaced in the controlled bath, and after a period of about 2 min. readings of the deflections of a Zeiss loop galvanometer were commenced with the instrument connected alternately to the axial and surface thermocouples by means of a mercury switch. The readings were continued at intervals of 10 sec. until the deflections became too small to be read accurately. The galvanometer was known to have a linear {current, deflection} characteristic. Since, moreover, a full-scale deflection was produced by a temperature-difference of about 3° C., it can be assumed without appreciable error that its deflections were proportional to the temperature-difference being measured.

The logarithms to base 10 of the readings thus obtained were plotted against time. If all the conditions of the theory were fulfilled, this gave two parallel straight lines whose slope determined

$$(\log_{10} \theta_1 - \log_{10} \theta_2) / (\tau_2 - \tau_1);$$

h^2 was then calculated from the equation

$$h^2 = 2.303 (\log_{10} \theta_1 - \log_{10} \theta_2) / \alpha_1^2 (\tau_2 - \tau_1).$$

α_1 being determined from equation (8) in the manner indicated above. A small error may arise in the determination of α_1 if the central thermocouple is not exactly on the axis of the cylinder. Fortunately a relatively large error in the position of this thermocouple only involves a small error in the value of α_1 . The possible magnitude of the error can be estimated as follows. Suppose that the central

thermocouple is as much as 2 mm. from the axis, which it is unlikely to be. For cylinders of the dimensions used the value of α_1 is approximately unity, so that, instead of

$$\theta_R/\theta_0 \text{ or } J_0(\alpha_1 R),$$

the quantity actually measured would be

$$J_0(\alpha_1 R)/J_0(\alpha_1 \times 0.2) \text{ or } J_0(\alpha_1 R)/0.99.$$

The error in the estimation of $J_0(\alpha_1 R)$ would thus be of the order of 1 per cent. But for the values of $(\alpha_1 R)$ with which we are concerned, namely about 2, a change of 3 per cent in the value of $J_0(\alpha_1 R)$ is caused by a variation of only one-half of 1 per cent in the value of $(\alpha_1 R)$. The value of α_1 deduced would thus be in error by about one-sixth of 1 per cent if the central thermocouple were as much as 2 mm. from the axis. This source of error has therefore been neglected.

It was assumed that there was no longitudinal flow of heat. The cylinders had a length approximately ten times their radius, and were insulated at the ends by rubber bungs, so that any longitudinal heat-flow must have been small. That it had no appreciable effect on the values of h^2 is shown by the results for water quoted below.

A small error must also be caused by the variation of the rate of heat-evolution of the concrete with temperature. If this error had been appreciable, there would have been a departure from linearity in the relation between τ and $(\log \theta_1 - \log \theta_2)$. This was not observed, and the error was accordingly neglected.

§ 4. TEST OF THE METHODS

The choice of a suitable standard material with which to test the apparatus presented some difficulty. Such a material should have at least one of its thermal constants accurately known, should be readily obtainable in a pure state, and should be without crystalline structure. No satisfactory solid substance having all these properties could be found. It was therefore decided to make a series of experiments with water.

The apparatus as described is not suitable for measurements on liquids, owing to the transfer of heat by convection. This difficulty was overcome by filling the tubes with a mixture of cotton wool and water. The presence of the cotton wool prevented convection, and had very little effect on the thermal constants of the mixture. Moreover its effect could easily be allowed for by making experiments with various densities of cotton-wool packing, and by extrapolating from the results obtained. In this way the thermal conductivity and diffusivity of water have been measured over the range of temperature from 20 to 50° C.

The experiments were made with distilled water, boiled immediately before use to expel any dissolved air, and with three different densities of packing of the cotton wool. The tubes were first filled with water, and the cotton wool was then added in small pieces and rammed down to the required density with a glass rod. It was found that by this procedure the specimens could be obtained free from entrapped air bubbles much more easily than by first packing the tube with the

cotton wool and then adding the water. The results are shown graphically in figures 3 and 4.

The present results for the conductivity can best be represented by the formula

$$k \times 10^3 = 1.39_2 (1 + 0.0023t).$$

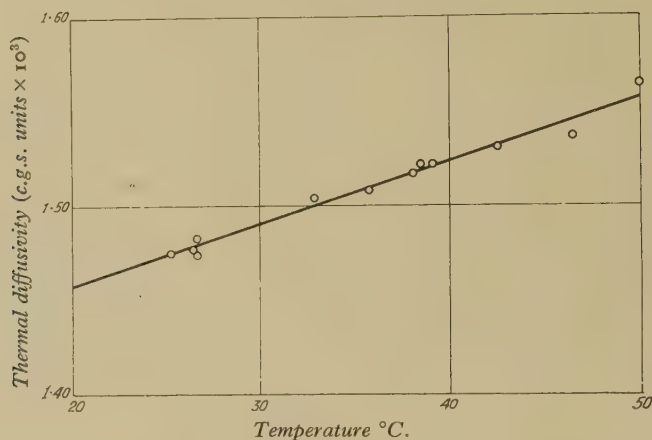


Figure 3. Thermal diffusivity of water.

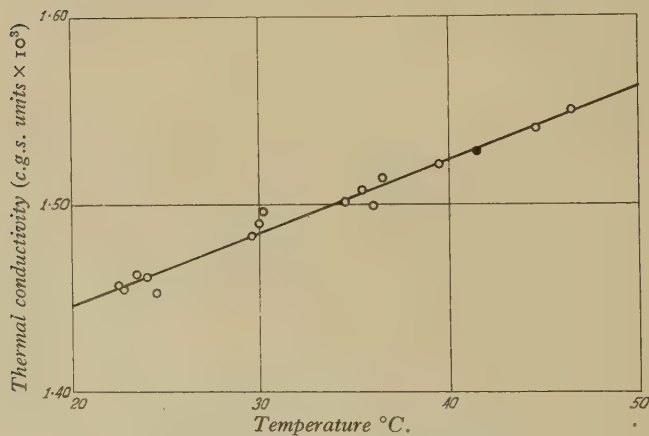


Figure 4. Thermal conductivity of water.

This is in excellent agreement with the results of Martin and Lang⁽⁶⁾, who found

$$k \times 10^3 = 1.39_4 (1 + 0.0023t).$$

Earlier measurements of the conductivity of water, which have been summarized in a table given by Martin and Lang, show a considerable divergence both in the value of k at 0°C. and in the temperature coefficient.

No previous direct measurements of the diffusivity of water appear to have been made. Since, however, both the specific heat and the density of water are accurately known, a comparison can be made between the values obtained for the diffusivity and those obtained for the conductivity.

At 20° C. the density of water is 0.998 and the specific heat is 1.000, while the corresponding values at 50° C. are 0.988 and 0.999. Thus at 20° C. we should find $k/h^2 = 0.988$, and at 50° C. $k/h^2 = 0.987$. Taking the mean values at 20° and 50° C. from figures 3 and 4, we find $k/h^2 = 1.008$ at 20° C., and $k/h^2 = 0.997$ at 50° C. Both these values are too large by about 1 per cent and it thus seems probable that the values of diffusivity are too low by this amount. This error cannot be caused by longitudinal heat-flow in the diffusivity specimens, since this would increase the rate of change of temperature and thus give a high value for h^2 . The error probably arises from the assumption of a linear relation between the diffusivity and the amount of cotton wool in the tube. This source of error will not arise in experiments with concrete, and it is therefore probable that both the conductivity and the diffusivity experiments give results which are correct to within 1 per cent.

§ 5. EXPERIMENTS ON CONCRETE

In the experiments on concrete there were certain points which required special attention. The measurements, as has already been stated, were made in the controlled bath and the temperature fluctuations of this bath caused by the operation of the relay, although small, were of sufficient magnitude to be appreciable in comparison with the temperature-differences which were being measured. It was therefore found desirable to suspend the operation of the automatic control while an experiment was being performed, and to adjust the heat-input to the bath by means of rheostats in the heater circuit, so that the correct rate of rise of temperature of the bath was maintained. For purposes of indication the thermocouple normally connected to the sensitive relay was connected instead to a mirror galvanometer, the deflection of which remained constant at or near zero when the correct rate of rise of temperature was achieved. By this method the rates of rise of temperature of the bath and of the controlling specimen could be made to agree very closely.

This suspension of the automatic control, although quite satisfactory as far as the thermal-conductivity experiments were concerned, introduced a further source of error into the diffusivity measurements. The diffusivity specimen, when replaced in the controlled bath after being cooled, caused a slight cooling of the bath, and consequently the temperatures of the specimen and the bath approached each other more rapidly than would have been the case if the bath-temperature had been unaffected by the introduction of the specimen, as it is assumed to be in the theory. Owing to the very short time available in the diffusivity experiments, it was not possible to compensate for this effect by alteration of the heat-input, and it was therefore necessary to correct the observed values of diffusivity.

It may reasonably be supposed that the error arising from this cause will be proportional to the ratio of the rate of change of the temperature of the bath to that of the test specimen. Thus if the change of deflection of the mirror galvanometer connected to the tank thermocouple during the course of an experiment be δd , and the corresponding change of deflection of the Zeiss galvanometer connected to the central thermocouple of the test specimen be δD , the error in the result will be

δd

δD

proportional to $\delta d/\delta D$. The constant of proportionality was determined by making two experiments with the same specimen but with slightly different rates of heat input to the tank, i.e. with different values of $\delta d/\delta D$. From the two apparent values of h^2 thus obtained it was found that a value of $\delta d/\delta D$ equal to 0.01 caused an error of 1.4 per cent in the diffusivity. In all subsequent experiments the value of $\delta d/\delta D$ was observed, and a proportionate correction was applied to the results. Since this was usually of the order of 1 per cent, and never exceeded 2 per cent, the final results cannot be seriously in error. A typical set of readings for a diffusivity experiment on a concrete specimen is given in table 1.

Table 1

Time (sec.)	Axial thermocouple		Surface thermocouple	
	Deflection D_1	$\log_{10} D_1$	Deflection D_2	$\log_{10} D_2$
0	86.4	1.9365	—	—
10	—	—	6.9	0.8388
20	67.7	1.8306	—	—
30	—	—	5.3	0.7243
40	52.5	1.7202	—	—
50	—	—	3.9	0.5911
60	40.5	1.6075	—	—
70	—	—	3.1	0.4914
80	31.2	1.4942	—	—
90	—	—	2.5	0.3979
100	24.1	1.3820	—	—
110	—	—	1.9	0.2788
120	18.8	1.2724	—	—
130	—	—	1.5	0.1761
140	14.5	1.1614	—	—
150	—	—	1.1	0.0414
160	11.4	1.0569	—	—

In figure 5 the values of $\log_{10} D_1$ and $\log_{10} D_2$ are plotted against time. It will be seen that two parallel straight lines are obtained; this shows that the conditions of the theory are fulfilled.

From figure 5 we obtain

$$\log_{10} \theta_t - \log_{10} \theta_{t+180} = 1.00$$

and

$$\log_{10} J_0(\alpha_1 R) = 2.944,$$

i.e.

$$J_0(\alpha_1 R) = 0.0879,$$

whence

$$\alpha_1 R = 2.241.$$

Therefore, since $R = 2.13$ cm. we have

$$h^2 = 0.01156.$$

This is the apparent value of h^2 uncorrected for temperature-changes in the tank during an experiment. In this experiment $\delta d/\delta D$ was equal to 0.013.

Hence the true value of h^2 is

$$0.01156 / (1.014 \times 1.013) \text{ or } 0.01136.$$

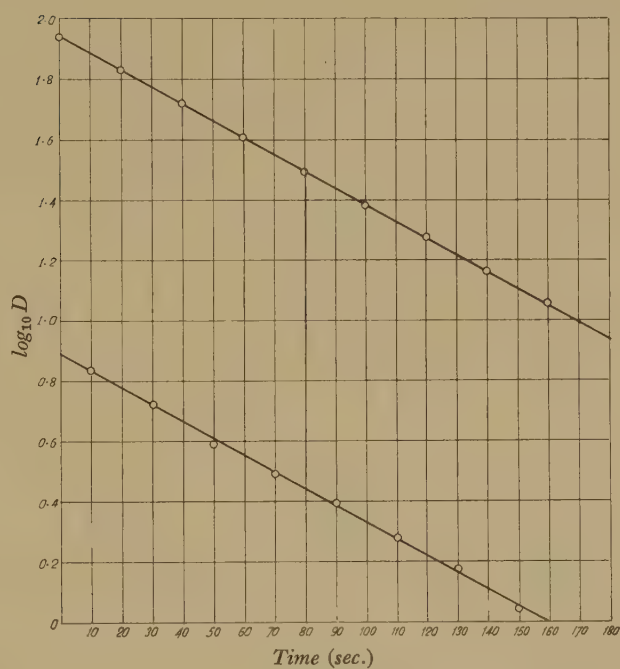


Figure 5.

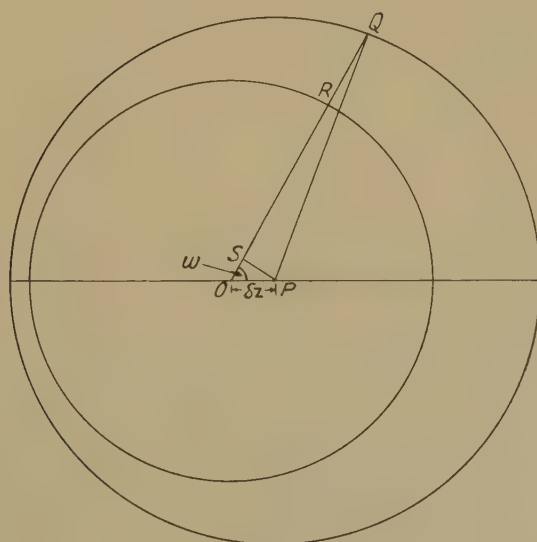


Figure 6.

The thermal constants of concrete will of course be influenced by a number of factors, such as the type and size of the aggregate used, the proportions of the mix, and the density of the concrete. Up to the present no attempt has been made to study these factors in detail, the preliminary experiments having been restricted to a siliceous aggregate, to normal and rapid-hardening Portland cements, and to a standard mix, namely cement, sand and water in the proportions of 1 : 6 : 0.6 by weight. In view of the dimensions of the specimens a small aggregate has been used, the particles ranging in size between $\frac{1}{100}$ in. and $\frac{1}{8}$ in., and being uniformly graded within these limits. The results for typical specimens are shown in tables 2 and 3.

Table 2. Normal Portland cement concrete. Density 2.11

Time after mixing (hours)	Tank-temperature (°C.)	Conductivity k	Diffusivity h^2	Specific heat s
4	18.6	0.00578	0.0110 ₄	0.248
6 $\frac{1}{2}$	19.8	0.00578	0.0110 ₇	0.247
25	33.0	0.00573	0.0110 ₉	0.245
31	35.1	0.00575	0.0110 ₉	0.246
48 $\frac{1}{2}$	40.0	0.00581	0.0112 ₅	0.245
55	41.1	0.00582	0.0112 ₄	0.245
72	43.3	0.00586	0.0113 ₅	0.244

It will be seen that with both normal and rapid-hardening Portland cements the thermal conductivity and diffusivity increase slightly with time, while the specific heat shows a slight decrease.

Table 3. Rapid-hardening Portland cement concrete. Density 2.13

Time after mixing (hours)	Tank-temperature (°C.)	Conductivity k	Diffusivity h^2	Specific heat s
4 $\frac{1}{2}$	20.9	0.00594	0.0112 ₅	0.248
7	22.3	0.00595	0.0113 ₀	0.247
13	30.0	0.00599	0.0113 ₁	0.248
24 $\frac{1}{2}$	38.6	0.00603	0.0114 ₅	0.247
31	41.4	0.00606	0.0115 ₇	0.246
48 $\frac{1}{2}$	45.6	0.00608	0.0116 ₈	0.245
55	47.0	0.00617	0.0117 ₈	0.246
72	49.1	0.00622	0.0118 ₈	0.246

The mean values of conductivity and diffusivity recommended by Davey and Fox, on the basis of a study of the work of a number of investigators, are 0.0045 c.g.s. units and 0.009 c.g.s. units respectively. The results now obtained are considerably higher than these values. The present results, moreover, show no sign of decreasing with time to the mean values for dry concrete. This is probably due to the fact that the specimens are almost completely sealed up inside the tubes, and there is no way of escape for moisture. The excess water which does not combine with the cement thus remains behind, keeping the concrete moist and consequently increasing the conductivity.

In this respect the present technique again imitates fairly closely the natural conditions, for during the setting period, when the shuttering is still in position and the surface of the concrete is usually covered, the loss of water by evaporation from a mass of dense concrete must be extremely small.

It is hoped to continue these experiments in order to find how the values of the thermal constants are affected by the other factors mentioned above. The variation is, however, expected to be small, and, in view of the approximate nature of the calculations of temperature-rise for which the constants are required, it is suggested that for the time being the values 0.006 c.g.s. units for the conductivity and 0.115 c.g.s. units for the diffusivity should be adopted. Certainly these values will be more accurate than those previously assumed. As regards the specific heat, the mean value obtained from the experimental results is 0.246. The value computed from the specific heats of the separate constituents of the concrete is 0.25, and it is therefore recommended that the value 0.25 be used.

§ 6. ACKNOWLEDGMENTS

In conclusion, the author wishes to express his thanks to Mr H. E. Beckett for much valuable advice and encouragement during the course of the work, and to the Director of Building Research, for permission to publish this paper.

REFERENCES

- (1) FOX. *Philos. Trans. A*, **232**, 43-461 (1934).
- (2) FOX. *Phil. Mag. Series 7*, **13**, 209-27 (1934).
- (3) DAVEY and FOX. *Build. Res. Tech. Pap.*, No. 15, Lond. (1933).
- (4) DAVEY. *Concr. constr. Engng*, **26** (10), 572-5 (1931).
- (5) CARSLAW. *The Conduction of Heat*, p. 115 (2nd ed. 1921).
- (6) MARTIN and LANG. *Proc. phys. Soc.* **45**, 523-9 (1933).

APPENDIX

HEAT-FLOW BETWEEN NON-COAXIAL CYLINDERS

Since it was difficult in practice to ensure that the two cylinders used in the conductivity experiments should be accurately coaxial, an approximate calculation of the error likely to be introduced by this assumption has been made.

Let R_1 and R_2 be the radii of the inner and outer cylinders respectively, and Z the distance apart of their axes, which are assumed parallel. If Z is small we can assume that the isothermal surfaces are cylinders, and that the radius r of any isothermal cylinder is connected with the distance z of its axis from that of the inner cylinder by the equation

$$z = (r - R_1) Z / (R_2 - R_1) \quad \dots\dots(10).$$

Consider a shell bounded by the isothermal cylinders whose radii are r and $r + \delta r$, and whose axes are distant z and $z + \delta z$ from that of the inner cylinder.

R_1, R_2

r

z

t, ω

The thickness t of the shell in a direction making an angle ω with the line of centres will be, to the first order in δr ,

$$\delta r \{1 + Z \cos \omega / (R_2 - R_1)\}.$$

 $\delta\theta$ δQ

If $\delta\theta$ is the temperature-difference across the shell and k the conductivity of the material, the heat-flow δQ per unit area across the shell in the direction ω is thus

$$-k\delta\theta/\delta r \{1 + Z \cos \omega / (R_2 - R_1)\}.$$

 Q

Integrating for all angles of ω we find that the total heat-flow Q through the shell per unit length is given by

$$\begin{aligned} Q &= -2 \int_0^\pi \frac{k \cdot \delta\theta \cdot r}{\delta r \{1 + Z \cos \omega / (R_2 - R_1)\}} \cdot d\omega \\ &= -\frac{2k(R_2 - R_1)}{\delta r} r \delta\theta \int_0^\pi \frac{d\omega}{Z \cos \omega + R_2 - R_1} \\ &= -\frac{2\pi k(R_2 - R_1) r \delta\theta}{\sqrt{\{(R_2 - R_1)^2 - Z^2\}}} \delta r. \end{aligned}$$

Since Q is independent of r , we can write

$$Q \frac{\delta r}{r} = -\frac{2\pi k(R_2 - R_1)}{\sqrt{\{(R_2 - R_1)^2 - Z^2\}}} \cdot \delta\theta,$$

which, on integration from R_1 to R_2 , gives

$$Q = \frac{2\pi k(\theta_1 - \theta_2)}{\log_e R_2 - \log_e R_1} \cdot \frac{R_2 - R_1}{\sqrt{\{(R_2 - R_1)^2 - Z^2\}}}.$$

This expression differs from that for coaxial cylinders only in the factor

$$\frac{R_2 - R_1}{\sqrt{\{(R_2 - R_1)^2 - Z^2\}}}.$$

With a value for Z of 0.2 cm.—which is greater than is likely to occur in practice—and with R_1 equal to 0.396 cm. and R_2 to 2.13 cm., this factor is equal to 1.007.

Thus the error in the conductivity measurements due to the two cylinders not being coaxial is not likely to exceed one-half per cent.*

* Since this paper was written it has been pointed out by Dr F. Garwood, of the Building Research Station, that the exact expression for the heat-flow between non-coaxial cylinders is

$$Q = 2\pi k(\theta_1 - \theta_2) / \log_e \frac{R_1 [R_2^2 - R_1^2 + Z^2 - \sqrt{\{(R_2^2 - R_1^2 + Z^2)^2 - 4R_2^2 Z^2\}}]}{R_2 [R_2^2 - R_1^2 - Z^2 - \sqrt{\{(R_2^2 - R_1^2 + Z^2)^2 - 4R_2^2 Z^2\}}}.$$

According to this formula, the error when $Z = 0.2$ cm. is 0.5 per cent, and this is in substantial agreement with the value of 0.7 per cent given by the approximate method.

ELECTRON ENERGIES AND EXCITATION IN THE HELIUM POSITIVE COLUMN

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ABSTRACT. The results of previous experimental investigations of the intensities of the spectral lines emitted from helium discharges are discussed, and a distribution function for the energies of the electrons is suggested in order to account for these results. The variation of the intensities of the lines with the pressure of the gas is then calculated, and curves are drawn representing the relative intensities of the various lines at different pressures. These curves are compared with those representing the observed variations of the intensities. The general agreement between the two sets of curves supports the conclusion that the distribution of the energies of the electrons in helium is of the form suggested. In this case the distribution may be expressed approximately by the formula

$$dN/N = (Ae^{-3y/2} + e^{-0.4y/2}) y^{\frac{1}{2}} dy,$$

where N is the total number of electrons of mean energy E_1 , dN is the number with energies lying between E and $E + dE$, A is a constant of the order of 5×10^{-3} , and y is E/E_1 .

It is then concluded that the distribution of the energies of the vast majority of the electrons in the helium positive column is determined by the process of diffusion and the mean loss of energy in elastic collisions with atoms of the gas; but that a small fraction 2×10^{-3} of the total number form a group with their energies distributed according to Maxwell's formula corresponding to the same mean energy. It is pointed out that this small group of electrons is of predominating influence in the helium discharge at high pressures as far as excitation and ionization are concerned.

§ 1. INTRODUCTION

IN recent years there have been many investigations^(1, 2, 3) of the variations of the intensity of the light emitted from the positive column of the helium discharge when the pressure of the gas is altered. These experiments have been carried out with both high-frequency and direct-current discharges in wide tubes, and they have been chiefly confined to the visible spectrum. Various methods of measuring the intensity of the light emitted have been adopted; for example, colour filters have been used in conjunction with photoelectric or selenium cells, and also the spectra have been photographed. There is good agreement between the results of all the experiments. The intensities of the lines were found to be directly proportional to the current, and to increase as the pressure of the gas was decreased from 40 mm. to about 0.5 mm. while the current was maintained constant. However, the most notable feature is the very rapid increase of intensity with pressure in the neighbourhood of 1 mm.

The general explanation of these results has been given previously^(1,2,3), but the theory may be explained briefly in the following way.

When a stream of electrons moves through a gas in a uniform electric field the mean energy of agitation E_1 may be expressed as a simple function of the ratio of the intensity of the electric force Z to the pressure p of the gas if E_1 is primarily determined^{(4)*} by the energy losses in elastic collisions with the atoms of the gas. The mean energy has been determined accurately by means of experiments on the lateral diffusion of a stream of electrons, and for a range of values of Z/p from about 1 to 2 the value of E_1 is almost exactly $2Z/p$ for helium when Z is expressed in volts per centimetre and p in millimetres. Thus the mean energies of the electrons in the uniform positive column at various pressures can be found by determining the ratios Z/p for those pressures. Further, it follows from Townsend's theory that the same processes obtain in the high-frequency luminous glow, and E_1 is also given for h.f. discharges when Z is the r.m.s. value of the force.

Now the excitation energy V of the various lines in the helium spectrum is of the order of 22 V., and this is much greater than the mean energies which lie between 2 and 6 V. Thus it follows that the energies of the electrons are distributed about the mean energy, so that only a small fraction of the total number of electrons have energies greater than V . Hence a small change in the value of E_1 causes a large change in the number of electrons with energies greater than V , which are capable of exciting the atoms of the gas. For example, the value of the mean energy is only doubled when the pressure is reduced from 40 mm. to about 0.5 mm., but the number of electrons with energies greater than V is increased about a thousand times. This results in a great increase in the intensity of the light at the lower pressures for a given current.

It is the purpose of this paper to suggest a distribution formula for the energies of the electrons in helium, and then to show how the observed variation of the intensity of the lines in the visible spectrum with the pressure of the gas in the discharge tube may be accounted for throughout the whole range of pressures investigated experimentally. The relative intensities of the most prominent lines have been measured accurately by Keyston by a spectrophotographic method at different pressures between 40 mm. and 0.32 mm., and these results will be compared with the relative intensities of the lines deduced theoretically.

§ 2. THE EXPERIMENTAL DATA

The intensities of the various lines measured by Keyston and published in his paper⁽³⁾ are given again, for purposes of comparison, in table I in which the intensity of the lines when the gas pressure is 7 mm. is in each case taken to be 100. These measurements are in good agreement with those found in the earlier investigations, when photoelectric cells and colour filters were used, throughout the

* The function depends on the mean free path L of the electrons in the gas at 1 mm. pressure, the average loss of energy λ in an elastic collision, and the distribution of the energies of the electrons about the mean. When all the energies are equal (1) $E_1 = L/\sqrt{(3\lambda)} \cdot Z/p$; and for a Maxwellian distribution $E_1 = L/\sqrt{(2.66\lambda)} \cdot Z/p$.

range of pressures from 40 mm. to about 4 mm. At pressures of about 0.5 mm. it is not easy to measure the electric force in the positive column accurately, and the values of Z/p (and consequently of E_1) for the pressures 0.78 and 0.32 which are given in the original table were there considered to be only approximate determinations. Now in the following calculations of the intensities of the lines it is very important to know the exact values of the mean energies of the electrons at these two pressures, and since the values of Z/p are not known they may be found by extrapolation.*

These estimated values of E_1 , together with the corresponding values of W_1 , the drift velocity⁽¹⁵⁾ of the electrons, are as follows:

$$p = 0.78, E_1 = 5.06 \text{ V.}, W_1 = 1.7 \cdot 10^6 \text{ cm./sec.}$$

$$p = 0.32, E_1 = 5.8 \text{ V.}, W_1 = 2.45 \cdot 10^6 \text{ cm./sec.}$$

§ 3. THE DISTRIBUTION FORMULA

The distribution of the energies of electrons in a gas under a uniform electric field is determined by processes, such as diffusion, which are different from those which set up the Maxwellian distribution. For very small values of the electric field, when the electrons are in thermal equilibrium with the gas atoms, the energy-distribution is Maxwellian; but when the mean energy increases, as a result of an increase in the electric force, the distribution changes continuously from the Maxwellian form to one which is determined by the process of diffusion. Formulae representing such a distribution have been given previously by Townsend, Druyvesteyn and others^(5,6,8,9), and the manner in which the distribution changes from the Maxwellian form with very weak fields to the diffusion form when the mean energy is of the order of 100 times that of the gas atoms has also been pointed out by Townsend⁽⁷⁾. This distribution may be expressed in the form

$$dN_1 = N_1 y^{\frac{1}{2}} e^{-0.55y^2} dy \quad \dots\dots(1), \quad N_1$$

where $y = E_x/E_1$, and N_1 is the total number of electrons with the mean energy E_1 , and dN_1 is the number with energies lying between E_x and $E_x + dE_x$. y
 E_x

This expression is obtained on the following assumptions. (i) That the mean free path L of the electrons in the gas at 1 mm. pressure is a constant, and independent of the energy E_x of the electrons; (ii) that the loss of energy by an electron in an elastic collision with an atom of the gas may be expressed as a constant fraction λ of the energy of the electrons, and that there are no collisions except of this kind— λ
i.e. the losses of energy in large amounts, such as would be required for excitation and ionization may be neglected; and (iii) that the mean energy of agitation of the electrons is large compared with that of the gas atoms.

* If the observed intensities of the various lines are plotted against the values of E_1 originally given the graphs are nearly straight lines, but they all show a sudden change of direction at a value of E_1 of about 4.7 V. By extrapolating the straight sections for greater values of E_1 the corrected values of the mean energy corresponding to the observed intensities may be found. These estimates may be checked by plotting various functions of E_1 , which are encountered below, against the pressure, and then extrapolating to the pressure 0.78 mm. and 0.32. The values of the functions at these points then determine E_1 .

For low values of Z/p such as those obtained in the positive column in helium and neon in wide tubes these conditions are sensibly fulfilled, and the distribution expressed in equation (1) has been applied in researches on the excitation of helium and neon in discharges^(1, 2, 3). However, it was found that the observed rate variation of the intensity of the light with pressure could not be accounted for by assuming this distribution formula for the electrons. A formula which gave a wider distribution was found necessary. On the other hand, the assumption of a Maxwellian distribution gave better agreement than the diffusion formula throughout the limited range of pressures investigated in these experiments, when the mean energy of agitation was less than 4 V. Further, under the same conditions a Maxwellian distribution was able to account for the observed rate of variation of the electric force with the gas pressure in the positive column in helium⁽¹⁰⁾. Now it was emphasized in that case that it is only to those electrons which have energies very much larger than the mean that Maxwell's formula need apply, and the energies of the electrons more nearly equal to the mean may be distributed in an entirely different way. Further, it is only a small fraction of the total number of electrons that have the high energies necessary to excite or ionize the atoms of the gas, so that it is only a small fraction of the total number of electrons that must be distributed according to Maxwell's formula in order to account for the experimental results. On the other hand, the results of Keyston show that the suitability of Maxwell's formula breaks down completely at low pressures less than 4 mm., i.e. with mean energies greater than about 4 V. In deducing the diffusion expression (i) the mean loss of energy of an electron of mass m in a collision with an atom of mass M is assumed to be a constant fraction λ of the energy E_x , and the variations of λ about the mean are neglected. Now when the ratio Z/p is low the coefficient λ is not a constant $2m/M$ but is more nearly represented by $(1 - E_1/E_0) \cdot 2m/M$, where E_0 is the mean energy of the gas atoms. This has been confirmed by the results of Townsend and Bailey on the motions of electrons in gases, and it shows that the effect of the energy of the gas atoms in collisions with electrons may not be neglected when Z/p is low, i.e. at high pressures. However, this variation of the energy loss about the mean loss may be regarded as the mechanism which sets up a Maxwellian distribution, and the lower the mean energy of the electrons the more important does this mechanism become. It is significant that at the higher pressures, when the mean energy of the electrons is low, the Maxwellian distribution is able to account for the observed changes both of light intensity and of electric force with the pressure of the gas. Again, collisions among the electrons themselves tend to set up a Maxwellian distribution of their energies.

Only experiments performed with comparatively high mean energies of the electrons, i.e. with pressures less than 1 mm., will enable the distribution of the energies of the main body of electrons to be found by these methods. For with high pressures, and consequently low mean energies, the excitation energies are about 6 or 8 times the mean energy, but with pressures of about 1 mm. the energies of the exciting electron are only about 3 or 4 times the mean. Consequently the number of electrons concerned in excitation or ionization is very much greater at

the lower pressures than at high pressures. If the distribution formula were known it would be possible, by making reasonable assumptions as to the probability functions of the various lines, to calculate the variation of the intensities of these lines as the pressure is reduced. Hence, by comparing the calculated intensity-variations with those found experimentally it is possible to test the validity of various distribution functions, and thus to find the formula which represents the distribution of the energies of the electrons in the discharge. The empirical formula which has been found in this way to account most satisfactorily for the experimental results may be expressed approximately in the following equation:

$$dN_1 = N_1 (2.07 f e^{-3y/2} + 0.7 (1-f) e^{-0.4y/2}) y^{\frac{1}{2}} dy \quad \dots\dots(2),$$

where

$$f = 1.882 \cdot 10^{-3},$$

so that $(1-f)$ is practically unity.

This equation may be regarded as expressing the fact that the energies of a small fraction $2 \cdot 10^{-3}$, of the total number of electrons are distributed according to Maxwell's formula, while the distribution of the energies of the vast majority of the electrons is represented by a formula very similar to the diffusion distribution of (1).

The mean energies of the two groups are the same, and it is the smaller group that is of predominating influence at the higher pressure as far as excitation and ionization in the positive column are concerned. It is suggested that this formula is valid over a very wide range of pressures, 0.32-40 mm. ($1 < Z/p < 4$) when f is practically constant. However it should be realized that in reality f is not actually constant, but is a function of the energies of the electrons and atoms. Thus when Z/p is practically zero or very small the mean loss of energy of the electron is zero, the distribution is Maxwellian, and $f=1$. When Z/p increases f decreases, and the process of diffusion begins to affect the distribution. Finally when Z/p is very large f vanishes and the distribution is entirely controlled by diffusion, on the assumption that only elastic collisions occur.

In order to calculate the relative intensities of any line at various pressures it is first necessary to consider the probability of excitation of that line by electron impact, which is a function of the energy of the electron that excites it.

§ 4. THE EXCITATION FUNCTION

There have been many experimental investigations^(11, 12, 13, 14) of the excitation of the helium atom by electron impact, and these experiments show that the probability of excitation increases from zero to a maximum value, when the energy of the electron is increased above the excitation energy V of the atom. The actual shape of the excitation function when plotted as a function of the energy E_x of the electron is different for the different lines, but there is a marked family likeness between the curves for those lines which belong to the ortho-helium system, and also between the curves for those which belong to the par-helium system.

For example, while the excitation curve for each state shows a maximum value corresponding to a certain energy E_m of the colliding electron, the sharpness of the

E_m

maximum depends on the system to which the lines belong. In general, lines belonging to the singlet system have excitation curves with broad maxima at high energy roughly corresponding to about 80 V., while the excitation curves of the triplet lines show sharp maxima at energies E_m of about 30 V. It is the differences in the form of the excitation functions of these lines which have approximate equal excitation energies that accounts for their different behaviour as the pressure of the gas in the discharge tube is changed. For the purposes of this investigation it is only necessary to find simple expressions which approximate to the actual forms of the probability-of-excitation curve determined experimentally. For instance, the excitation curves of those lines which rise sharply to a maximum value may be represented by the equation

$$P = k, \quad V < E_x < \infty \quad \dots\dots(3),$$

where P is the excitation function and k is a constant.

For example, such lines are $\lambda 5016$ and $\lambda 4713$.

Moreover, for many triplet lines we may take

$$\begin{aligned} P &= k (E_x - V)/E_x, & V < E_x < E_m \\ P &= 0 & E_x > E_m \end{aligned} \quad \dots\dots(3').$$

This form is suitable for lines such as $\lambda 5876$, $\lambda 3889$. Now, owing to the form of the distribution curves expressed in equation (2), the number of electrons with energies greater than any given value V diminishes rapidly as V increases. When V is about 5 times the mean energy E_1 the integration of the formula (2) between the limits V and $3V/2$ is practically identical with integration between the limits V and infinity. Hence the exact shape of the probability curves for values of the energy of the electrons greater than $3V/2$ is not of much importance because in this case the important part of the curves is that in the immediate neighbourhood of the excitation energy. Unfortunately, the experimental determination of the form of the probability functions of the various lines in the immediate vicinity of their excitation energies is beset with great difficulty. The determinations are only approximate for this region, and there is no exact agreement in the values found by various observers.

However, it is interesting to note that when the mean energy of the electrons in the discharge is very low (< 3 V.) the number of electrons with energies greater than, say, 25 V. may be neglected in comparison with the number with energies greater than, say, 23 V. Thus in this case the only important range of the excitation function of the various lines is that lying between the energies corresponding to 23 and 25 V. Now, as far as can be seen from the experimental determinations the excitation-probability curves for all the various lines have the same shape within this narrow range. Hence it follows that the behaviour of all the lines in the visible spectrum will be practically the same if their excitation energies are not very different. This accounts for the fact that the intensities of all the lines in the radiation from the helium glow discharge, which were measured by Keyston, increased in exactly the same ratio when the pressure of the gas was reduced from

40 to 7 mm. corresponding to a change of mean energy of the electron from 2.58 to 3.85 V.

However, at the lower pressures, when the mean energy of the electron is greater than 3.85 V., the number of the electrons with energies greater than say 25 V. can no longer be neglected in comparison with the number with energies greater than 23 V. Thus in this case it is necessary to take into consideration the different forms of the excitation function for the different lines.

§ 5. THE CALCULATION OF THE RELATIVE INTENSITIES OF THE LINES AT DIFFERENT PRESSURES

When an atom is in an excited state, in general, more than one transition to a lower level is possible. In the case of the helium lines under consideration, and given in table 1, the only exception is in the transition $2^3S - 3^3P$ (λ 3889), as this is the only one allowed from the 3^3P level. However, in each case the number of transitions from any given excited state is proportional to the number of atoms in that excited state, though only in the case λ 3889 is the number of transitions equal to the number of excited atoms.

However, in this paper only the relative intensities of each of the lines at various gas pressures are being considered, and the relative intensities of any given line are proportional to the relative numbers of the excited atoms at those pressures.

The intensity of the light of a certain wave-length which is emitted from the glowing gas is proportional to the number of atoms in a certain excited state, and it does not depend on the way in which that state has been excited. Now an atom may be put into a given excited state by any of the following processes: (i) a single collision with an electron, (ii) two successive collisions involving two electrons, (iii) the emission of radiation by the atom when in a higher excited state, (iv) the recombination of a helium positive ion and an electron. However, in those cases⁽¹⁾ in which the intensity of the radiation emitted from the helium positive column has been measured it has been found to be directly proportional to the current, and this result is in agreement with the experiments of Lees⁽¹⁴⁾, in which the gas was excited by a homogeneous beam of electrons from a filament. Thus it follows that the atoms are not excited by any process requiring a double electron impact. Again, for large quantum numbers the classical rule governing transitions between various states is approximately valid. Thus the intensity of a line of frequency ν , measured by the number of quanta emitted per second by the atoms due to transitions between states which differ in energy by $h\nu$, is proportional to ν^3 , so that the probability of successive changes in energy levels involving the emission of low-frequency radiation is low, and it may be neglected in comparison with the probability of transitions involving the emission of lines of the shortest possible wave-length. Further, it has been shown previously^(2,16) that no appreciable radiation is emitted from a positive column of a discharge as a result of the process of recombination. The most favourable conditions for recombination in a dis-

charge tube obtain in the Faraday dark space, and no appreciable light is emitted from this region. There is no recombination in the body of the glowing gas in the positive column as the ions and electrons recombine at the walls of the tube towards which they are driven by the action of diffusion and the radial electric field set up by the charge in the gas.

Thus it may be assumed that the excitation of the radiation emitted from the positive column in the discharge is due principally to the single collisions of the atoms of the gas with electrons of high energy.

Consider the uniform positive column in a wide cylindrical discharge tube, and let the total number of electrons in 1 cm. length of tube be N_1 . Then if the energies of the electrons are distributed according to equation (2) the number dN_1 of electrons with energies lying between E_x and $E_x + dE_x$ is proportional to

$$(Be^{-3y/2} + e^{-0.4y^2}) y^{\frac{1}{2}} dy,$$

where B is a constant equal to $5.38 \cdot 10^{-3}$.

If n is the number of atoms per cm^3 at a pressure of 1 mm. and q_i is the cross section of an atom for excitation to a given state, then the number of excitations of that state per sec. per cm. of column due to collisions with electrons of energy p_1 in the gas at pressure p_1 is proportional to

$$dN_1 p_1 n q_i (2eE_x/m)^{\frac{1}{2}} \quad \dots\dots(4).$$

Now if q_k is the gas-kinetic cross section of an atom, then $q_i = P q_k$, where P is the probability of excitation by electron impact. It is now necessary to consider separately the two forms of the function P as given in equations (3) and (3').

(i) Let $P = k$ when $E_x > V$.

Then the total number I_1 of excitations per second is obtained by integrating the expression (4) from V to infinity. Thus

$$I_1 = \int_V^{\infty} C p_1 E_1^{\frac{1}{2}} (Be^{-3y/2} + e^{-0.4y^2}) y dy,$$

where C is a constant equal to $0.8 N_1 k n q_k (2e/m)^{\frac{1}{2}}$. Hence the intensity I_1 is proportional to

$$N_1 p_1 [B(V + 2E_1/3) 2E_1^{-\frac{1}{2}}/3 e^{-3V/2E_1} + 1.25 E_1^{\frac{1}{2}} e^{-0.4(V/E_1)^2}] \quad \dots\dots(5).$$

(ii) Now consider the alternative form of the function P given in equation (3'). The number of excitations per second is given by

$$I_1 = \int_V^{\infty} C p_1 (1 - V/E_1 y) y^{\frac{1}{2}} (Be^{-3y/2} + e^{-0.4y^2}) dy,$$

so that in this case the intensity I_1 is proportional to

$$N_1 p_1 \left[4B/9 E_1^{\frac{1}{2}} e^{-3V/2E_1} + 1.25 E_1^{\frac{1}{2}} e^{-0.4(V/E_1)^2} - 0.79 \sqrt{\pi} \cdot V E_1^{-\frac{1}{2}} \frac{2}{\sqrt{\pi}} \int_{\xi}^{\infty} e^{-\xi^2} d\xi \right] \quad \dots\dots(5'),$$

where $\xi = 0.648 V/E_1$.

The value of the integral in expression (5') can be obtained from tables⁽¹⁷⁾. Owing to the presence of this integral the function represented by (5') does not increase with E_1 as rapidly as the expression (5). Thus the form of the excitation function given in equation (3) is adopted for calculating the intensities of those lines which increase very rapidly as the pressure is diminished, such as the lines $\lambda 3188$, $\lambda 5016$ and $\lambda 4713$, while the form of P given by equation (3') may be adopted in the case of the lines $\lambda 5876$, $\lambda 6678$, $\lambda 3889$ and $\lambda 4471$. Let the two values of I_1 given at (5) and (5') be represented by

$$p_1 N_1 \phi(E_1).$$

 ϕ

Then the ratio of the intensities of a line at the two different pressures p_1 and p_2 is given by

$$I_1/I_2 = p_1 N_1 \phi(E_1)/p_2 N_2 \phi(E_2).$$

When the current is the same at both pressures then $N_1 W_1 = N_2 W_2$, so that

$$I_1 = I_2 W_2 p_1 \phi(E_1)/W_1 p_2 \phi(E_2) \quad \dots\dots(6).$$

The values of the function ϕ can be calculated for any value of E_1 , that is, of p_1 . Thus if the intensity I_2 of any given line at a pressure p_2 equal to 7 mm. is taken to be 100, then the intensity I_1 at any other pressure p_1 can be found from equation (6).

These calculated values for the relative intensities of the lines are given in table 1, in which the form of excitation function and the value of the excitation potential V for each line also are given.

Table 1. The intensities of the helium lines calculated from equation (6)

Pressure of gas in discharge	$\lambda 5876 \text{ } 2^3\text{P} - 3^3\text{D}$ $V = 22.96$ $P = k(E_x - V)/E_x$		$\lambda 4471 \text{ } 2^3\text{P} - 4^3\text{D}$ $V = 23.62$ $P = k(E_x - V)/E_x$		$\lambda 3889 \text{ } 2^3\text{S} - 3^3\text{P}$ $V = 22.89$ $P = k(E_x - V)/E_x$		$\lambda 3188 \text{ } 2^3\text{S} - 4^3\text{P}$ $V = 23.59$ $P = k$		$\lambda 4713 \text{ } 2^3\text{P} - 4^3\text{S}$ $V = 23.4$ $P = k$		$\lambda 5016 \text{ } 2^1\text{S} - 3^1\text{P}$ $V = 22.97$ $P = k$		$\lambda 6678 \text{ } 2^1\text{P} - 3^1\text{D}$ $V = 22.96$ $p = k(E_x - V)/E_x$		Z/p^\dagger
	Observed*	Calculated	Observed*	Calculated	Observed*	Calculated	Observed*	Calculated	Observed*	Calculated	Observed*	Calculated	Observed*	Calculated	
40	12	5	10	7	9	5	—	9	—	7	13	8	12	5	1.29
30	19	11	18	12	17	11	—	17.5	—	12	21	19	19	11	1.38
20	34	16	27	23	27	16	—	31	—	23	35	29	33	16	1.51
13	58	26	50	60	50	26	46	70	48	60	58	57	57	26	1.73
7	100	100	100	100	100	100	100	100	100	100	100	100	100	100	1.94
4	148	120	220	130	163	120	220	150	220	130	155	120	145	120	2.10
1.5	252	157	540	300	334	156	616	360	594	360	418	310	261	157	2.50
0.78	340	450	675	600	367	400	920	920	772	900	668	750	340	450	2.9
0.32	187	540	585	560	550	500	1200	1165	868	1100	1600	1100	303	540	3.85

* Experimental data after Keyston⁽³⁾.

† Z is the r.m.s. value of the force in the h.f. discharge.

Some typical results are also represented in the curves of figures 1 to 4. The ordinates represent the intensities of the various lines when their intensities at a

pressure of 7 mm. are taken to be 100, and the abscissae represent the mean energy of agitation of the electrons. The corresponding pressures also are marked. The different behaviour of the various lines is well illustrated by the curves; thus intensities of some of the lines continue to increase as the pressure is diminished while other lines become fainter at the lowest pressures.

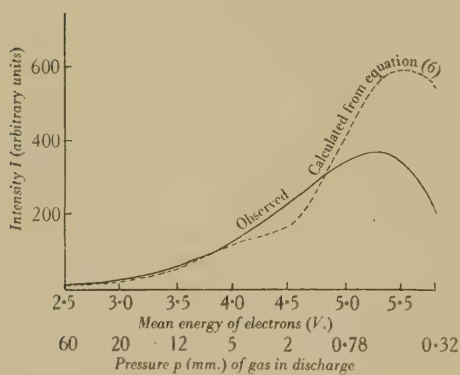


Figure 1. $\lambda 5876\ 2^3P-3^3D$; $\lambda 6678\ 2^1P-3^1D$.

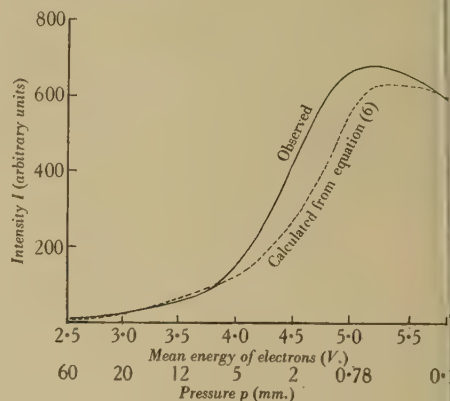


Figure 3. $\lambda 4471\ 2^3P-4^3D$.

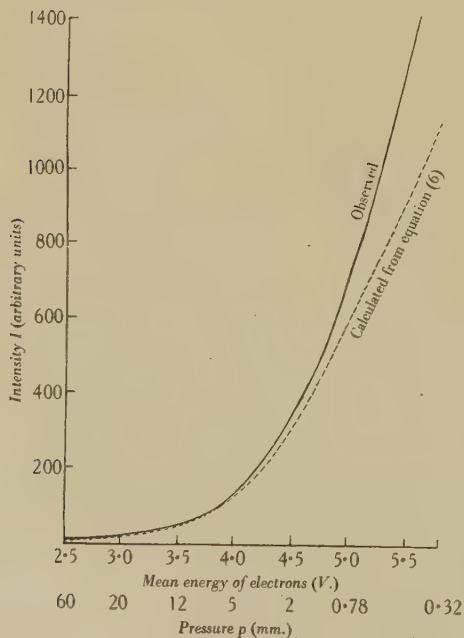


Figure 2. $\lambda 5016\ 2^1S-3^1P$.

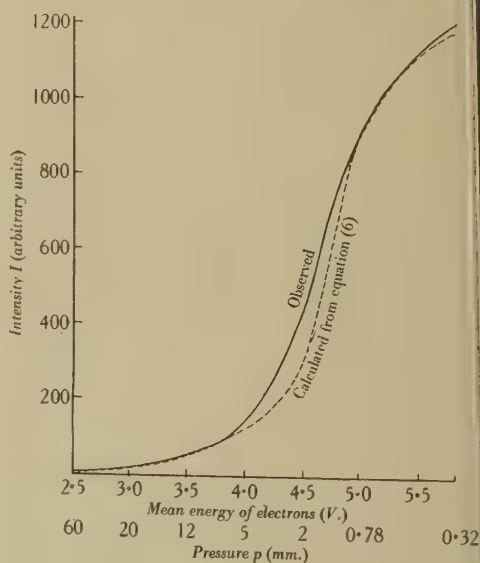


Figure 4. $\lambda 3188\ 2^3S-4^3P$.

§ 6. CONCLUSION

The curves show that there is a general agreement between the calculated and the observed variation of the intensity of the spectral lines as the pressure of the gas is altered. This result then supports the conclusions regarding the nature of the

distribution of the energies of the electrons which were arrived at in § 3. However, the agreement is not perfect and there are many causes which might give rise to the discrepancies between the theoretical and experimental curves. Firstly, as was pointed out above, the exact nature of the excitation functions of helium in the immediate neighbourhood of the excitation potentials of the various states is unknown; but there are theoretical and experimental considerations which indicate that the simple formulae of equations (3) and (3') are reasonable expressions of these functions, at least as far as their application in this case is concerned. Again, the variation of the mean free path of the electrons with their velocity—the Townsend-Ramsauer effect—was neglected in the derivation of the distribution formula. The mean free path L , at 1 mm. pressure, of electrons with various energies has been measured by Townsend's method⁽⁴⁾ at low velocities and by Ramsauer's method⁽¹⁸⁾ at high velocities, and the variation may be seen from the following table 2:

Table 2

E_x (V.)	1.85	3.7	5.2	10.7	15.8	19.2
L (cm. $\times 10^{-2}$)	4.8	5.2	5.5	6.7	8.3	9

This variation of the mean free path will not alter the form of the expression for the distribution but only the numerical coefficients in it. That is, the width of the distribution will be affected by the changes in L . In the case in which the free path diminishes as the energy of the electron is increased, the distribution would tend to become narrow. This effect occurs in argon, where the mean free path diminishes when the energy of the electron increases up to 10 V., and MacCallum, Klatzov and Keyston⁽¹⁹⁾, from a study of the continuous spectrum of that gas, have been led to the conclusion that the distribution in it is very narrow. Alternatively, table 2 shows that in helium L increases with E_x , so that the proportion of faster electrons is increased. This may account for the fact that a numerical coefficient 0.4 in the exponent in the distribution formula (2) gives better agreement in the above curves of relative intensities than does the theoretical value 0.55, which is obtained on the assumption that the mean free path is independent of the velocity. Further, a modification of the form of the distribution formula is required owing to the variations of the fractional loss of energy at a collision about the mean loss. Townsend has pointed out previously that the actual distribution is wider than that expressed by the simple diffusion expression (1) as due to this effect alone. However, the widening of the distribution from these causes is to some extent offset by the reduction in the number of fast electrons due to collisions resulting in excitation and ionization in which large losses of energy occur. On the other hand the maximum efficiency of ionization in helium by 100 V. electrons is only about 10 per cent and it is much less for excitation.

The original experiments on the motions of electron gases were interpreted⁽¹⁵⁾ on the basis of the older kinetic theory in which the collision between electrons and atoms of the gas were considered to resemble those between uncharged elastic spheres. Consequently the scattering of the electrons in collision with the atoms of

helium was considered to be uniform. However, the scattering of electrons in helium is not perfectly uniform; but the angular distribution of the scattered electrons is not very different from that which obtains in the case of uniform scattering, so that no great error is introduced from this cause. Non-uniform scattering would have to be taken into consideration if the mean energies E_1 were calculated from the measured ratio Z/p ; it should be emphasized, however, that the values of E_1 used in the calculations were not deduced from the values of Z/p but were the observed values found in the experiments of Townsend and Bailey for the corresponding values of Z/p .

Further, it should be realized that the only theoretical distribution formula possible under the conditions laid down in § 3 is that expressed⁽⁶⁾ in equation (1). On the other hand, equation (2) merely gives an expression with which it is possible to calculate the variation of the intensities of the spectral lines and of the force⁽¹⁰⁾ in the positive column of high-frequency and direct-current discharges in helium, and to find general agreement between the calculated rates of variation and those determined experimentally. This result supports the contention that when $Z/p < 4$ the actual distribution formula for the energies of the electrons in helium, and most likely in the other monatomic gases, is that given in equation (1) but that it is essential to take into consideration the variation of the mean free path of the electrons with velocity.

REFERENCES

- (1) TOWNSEND, J. S. E. and JONES, F. LLEWELLYN. *Phil. Mag.* **11**, 679 (1931) and **12**, 81 (1931).
- (2) TOWNSEND, J. S. E. and PAKKALA, M. H. *Phil. Mag.* **14**, 414 (1932).
- (3) KEYSTON, J. E. *Phil. Mag.* **16**, 625 (1933).
- (4) TOWNSEND, J. S. E. and BAILEY, V. A. *Phil. Mag.* **46**, 657 (1923).
- (5) TOWNSEND, J. S. E. *Phil. Mag.* **9**, 1145 (1930).
- (6) DRUYVESTEYN. *Physica*, **10**, 61 (1930); *Physica*, **1**, 1003 (1933).
- (7) TOWNSEND, J. S. E. *Phil. Mag.* **16**, 729 (1933).
- (8) DAVYDOV, B. Z. *Phys. Sowjet*, **8**, 1, 59 (1935).
- (9) MORSE, P. M., ALLIS, W. P. and LAMAR, E. S. *Phys. Rev.* **48**, 412 (1935).
- (10) JONES, F. LLEWELLYN. *Phil. Mag.* **15**, 958 (1933).
- (11) HUGHES, A. LL. and LOWE, P. *Proc. roy. Soc. A*, **104**, 480 (1923).
- (12) HANLE, W. *Z. Phys.* **61**, 94 (1929).
- (13) MICHELS, W. C. *Phys. Rev.* **36**, 1363 (1930).
- (14) LEES, J. H. *Proc. roy. Soc. A*, **137**, 173 (1932).
- (15) TOWNSEND, J. S. E. *Motions of Electrons in Gases*. (Clarendon Press.)
- (16) ——— *Electricity in Gases*.
- (17) BURGESS. *Trans. roy. Soc. Edinb.* **39**, 320 (1900).
- (18) RAMSAUER, C. and KOLLATH, R. *Ann. Phys.* (5), **12**, 529 (1932).
- (19) MACCALLUM, S. P., KLATZOV, L. and KEYSTON, J. E. *Phil. Mag.* **16**, 193 (1933).

DISCUSSION

Dr R. WINSTANLEY LUNT and Mr C. A. MEEK. (1) The distribution formula. The author does not give the formal derivation of the distribution formula which he now advances. Emeléus, Cowan and Brown* were able to account for the relative intensities of the lines $\lambda\lambda$ 5016, 4713 in the positive column and in the negative glow on the assumption of a Maxwellian electron-energy distribution in each of these zones. There are experiments on positive-column discharges in many gases for which Langmuir probe data indicate that the distribution is sensibly Maxwellian. (2) The excitation functions. Whilst the exact shape of the excitation functions in the neighbourhood of the critical potential is difficult to determine experimentally, the theoretical calculations of the excitation functions in helium are for the most part in agreement with the experimental determinations of Lees†; furthermore, it would be hard to find in these calculations‡ any justification for the particular approximate expressions selected by the author. The author points out that the excitation functions for lines belonging to the singlet system are characterized by broad maxima, whilst those of the triplet systems show sharp maxima. For "those lines which rise sharply" he suggests that the excitation function can be represented by his equation (3) and cites as an example λ 5016; this however is a singlet line $3^1P - 2^2S$, and its excitation function rises slowly to a broad maximum at about 100 volts.‡ Further, the author points out there is a "marked family likeness" between the curves belonging to a single system, but he has selected different approximate expressions for the excitation functions of two levels belonging to the same system, 3^3P [$P = k(E_x - V)/(E_x)$], and 4^3P ($P = k$). (3) Conclusion. Whatever may be the truth about the validity of the distribution function proposed by the author, his arbitrary selection of different approximate expressions for the excitation of lines of the same system, and of expressions which do not approximate sufficiently to the experimental data, tends to destroy, we believe, in a great measure the evidence now adduced by him in support of this distribution.

AUTHOR'S reply. (1) The distribution formula. With regard to the paper by Emeléus and others, the authors themselves state "we find that the distribution of velocity of electrons is not Maxwellian in the negative glow", and they make no mention of any conclusions regarding the distribution of energies in the uniform positive column over any range of pressures. Again, if we refer to a later paper§ by the same authors, also on probe measurements of the distributions in a helium discharge, we find no evidence presented there which indicates that the distribution in the uniform positive column is Maxwellian, and the authors do not suggest such a conclusion.

(2) Excitation functions. It was pointed out in § 4 that the steepness of the excitation curve is only important near the critical potential, owing to the low mean

* Emeléus, Cowan and Brown, *Nature*, Lond., **127**, 593 (1931); Cowan, Thesis, Belfast, 1931.

† Massey and Mohr, *Proc. roy. Soc. A*, **132**, 605 (1931); **140**, 613 (1933).

‡ Lees, *Proc. roy. Soc. A*, **137**, 173 (1932).

§ Emeléus, Brown and Cowan, *Phil. Mag.* **17**, 146 (1934).

energies of the electrons in the positive column and the narrowness of any reasonable distribution, so that a broad maximum in the curve at about 80 V. is of negligible consequence. Also in the relevant range of energy V to $3V/2$ the general distinction between the two systems of lines is not very pronounced, the marked family likeness for lines of the same system being more noticeable for energies greater than about 30 V. The excitation curve for the line $\lambda 5016$ (see Lees⁽¹⁴⁾) may be well represented by the equation $P = k(E_x - V)$ when $E_x < 80$ V. However, when this expression is used, the relative numerical values of the integral differ little from those of the integral (5), but as the expression itself is more complicated the simpler one of equation (5) is used as a sufficient approximation. The following are the reasons which lead to the adoption of the same formula, $P = k(E_x - V)/E_x$, to represent the initial stages of the excitation curves for the lines $\lambda 5876$, 3889 , 6678 , it being remembered that $P = 0$ when $E_x > V_m$ for the two triplets, $\lambda 5876$ and 3889 , and that k depends on their respective atomic cross-sections. Now the change in intensity of any line emitted from the helium positive column when the pressure of the gas is altered depends on its excitation potential, on the shape of its excitation curve in the initial range 23 to about 30 V., and on the mean energies and distribution function of the electrons. When the behaviours of two lines emitted from the same tube are being compared the last two factors are the same for both lines, so that any difference in their behaviour must be accounted for by differences in excitation potentials and curves. But the lines $\lambda\lambda 5876$, 6678 have practically the same excitation potentials and almost identical behaviour throughout the whole range 40 mm. to 0.8 mm. Hence it follows that the excitation curves of these lines have the same form within the relevant range of energies although one line is a triplet and the other a singlet. Also, the critical potential and the general variation of intensity is nearly the same for $\lambda 3889$ as for these two lines, so that the same function P was adopted. Hence it is considered that, within this range, the approximations given and discussed in § 4 of the paper are reasonable, and are not so much in error as to throw grave doubt on the validity of the results derived from them.

DEMONSTRATION

AN EXPERIMENT ILLUSTRATING THE SUPPORT OF A WEIGHT BY A VERTICAL TUBE CONTAINING SAND, THE LOWER END BEING COVERED BY A THIN MEMBRANE*

Demonstration given by Major C. E. S. Phillips, O.B.E., February 7, 1936

THIS demonstration formed part of a series of experiments shown by me at the Royal Institution in 1910 to illustrate a discourse there upon "Electrical and other properties of sand".

Dry sand emitted from a nozzle and falling upon a horizontal surface forms a cone, the angle at the base of which is 35° . It follows that sand flowing into a metal tube closed at the lower end first forms such a cone the base of which is limited by the diameter of the tube, so that if further sand enters the tube its particles roll down the slope of the cone first formed. As the tube fills up it may therefore be regarded as containing the original cone at the lower end and successive layers of particles which arrange themselves so as to preserve the original angle of slope, viz. 35° with the horizontal.

If such a column be gently tapped so as to pile or lock the grains and a vertical downward force be applied to the sand column, it is seen that this force is so resolved that only a small fraction of it reaches the cone at the base of the tube. If the walls of the tube are rigid, considerable weights can be thus supported by the column, owing to increased friction between the sand and the inner surface of the tube, it being only necessary to close the lower end with a thin membrane which is capable of supporting little more than the weight of the small cone of sand in contact with it.

In order to show this I have arranged a flanged vertical brass tube open at both ends, which projects through an arm of a kind of gallows. The diameter of the tube is 0.5 in. and the lower end is closed by a piece of cigarette paper held in position by means of a rubber ring. Enough white sand is now poured into the tube to stand about 3 in. above the thin paper. The tube is then gently tapped with a light hammer and a loose plunger is inserted from the top end carrying a cross piece with a ring at each end. An attempt to suspend Dr Ferguson from the rings will be made. It will appear as though his weight (21 st.) is supported by the thin cigarette paper.

The experiment was successfully carried out.

* See also a paper by J. H. Shaxby and J. C. Evans on "The variation of pressure with depth in columns of powders", *Trans. Faraday Soc.* **19**, Part 1 (May, 1923).

REVIEWS OF BOOKS

*Faraday's Diary: being the Various Philosophical Notes of Experimental Investigation made by Michael Faraday, D.C.L., F.R.S., during the years 1820-62.** Vol. 5 (Sept. 6, 1847-Oct. 17, 1851), pp. xiii + 456; vol. 6 (Nov. 11, 1851-Nov. 5, 1855), pp. xiv + 495; vol. 7 (Nov. 24, 1855-March 12, 1862), pp. xvii + 465; Index, pp. 64. (London: G. Bell and Sons.) Seven volumes and index. £12. 12s. the set.

In these last three volumes of the *Diary* we find, among other things, the details of Faraday's experiments on the magnetism of flame and other gases, and of his work on the behaviour of crystals in the magnetic field—the investigation of “magnecrystallic action” which is the subject of a well-known tribute from Tyndall to his predecessor. There is also the extensive development of the method of representing magnetic fields by lines of force, illustrated by fine reproductions of some of Faraday's filings maps. The last volume contains a full account of observations on the properties of precipitated gold; these are no doubt well known to physical and colloid chemists, but many physicists will be surprised to discover the extent and variety of Faraday's experiments with gold sols.

Of greater general interest, however, are the entries that relate to Faraday's protracted search for a connexion between gravity and electricity, and others which show his continued preoccupation with the relation between light and electromagnetism. In fact there can be no doubt that Faraday, though in the years under review he may be said to have passed the zenith of his career as an *experimental* philosopher, was nevertheless doing much to shape a general electromagnetic theory of light. Here is a typically significant passage (§ 14233, January 19, 1856): “Still, it is not absolutely certain that magnetic propagation, if in an (or the) ether, must be as quick as light, though it is likely.”

Of more special interest to physicists of a later generation are Faraday's experiments on the light from a source situated in a strong magnetic field. It has been generally known for some time, from the writings of Bence Jones, Maxwell and Silvanus Thompson, that these were the last experiments that he undertook; they are described in the closing passages of the *Diary*, and Faraday was in his 71st year when he entered them. It is perhaps less well known that he had attempted similar experiments almost nine years earlier. Thus (May 16, 1853, §§ 13053 *et seq.*): “In regard to the possibility of the Magnetic force affecting (*sic*) a change in the character of rays *emanating* from an object place[d] in the center of an intense magnetic field . . . the flame examined whilst submitted to the intermit[t]ed action of the magnet. Its light examined by the prism shewed no sensible difference whether the magnetism was on or off. It shewed no difference when examined in various ways by polarizers, i.e. Nicol's prisms.”

It is worth while stressing here the two respects in which this work is absolutely typical of Faraday's methods of research. In the first place, in all his experiments on light it was almost a matter of routine to test for polarization effects. Secondly, to quote Tyndall (*Faraday as a Discoverer*, p. 89), “One great source of his success was the employment of extraordinary power . . . he never accepted a negative answer to an experiment until he had brought to bear upon it all the force at his command.” Thus we see from the closing passages of the *Diary* how, having acquired a new Steinheil spectroscope, he applied it at once in the repetition of an experiment abandoned nine years earlier.

It is evident therefore that only the inadequacy of the technical resources of his time prevented Faraday from anticipating at least a part of Zeeman's magneto-optical dis-

* Vols. 1-4 were reviewed in these *Proceedings*, 45, 358 (1933) and 46, 484 (1934).

coveries. Zeeman, who inscribed his *Researches in Magneto-Optics* "to the Memory of Michael Faraday", was at first unaware of Faraday's unsuccessful attack upon the same problem. He has however recorded that at a later stage he was encouraged to persevere in his own attack by discovering that Faraday had considered the experiment worthy of trial.

In an *Encyclopaedia Britannica* article (reprinted in vol. 2 of his collected papers) Maxwell referred to Faraday's "concentration of his efforts in seeking to identify the apparently different forces of nature, his far-sightedness in selecting subjects for investigation, his persistence in the pursuit of what he set before him, his energy in working out the results of his discoveries, and the accuracy and completeness with which he made his final statement of the laws of the phenomena".

For evidence of these qualities we need look no further than the pages of the *Experimental Researches*, but many of them are seen in greater perfection in the *Diary*. We have therefore every reason to be grateful to the Managers of the Royal Institution for the great service they have done in giving the *Diary* to the public, and for giving it in so handsome and dignified a form. Credit must here be given also to the publishers and the Cambridge University Press for their shares in the production.

Mr Martin is to be warmly congratulated upon the wholly admirable way in which he has edited Faraday's manuscript. It must have been an onerous as well as a difficult task, and it is not altogether surprising that a faintly plaintive note is to be detected at the end of his preface to vol. 7. He may however derive some satisfaction from the thought that the task was well worth doing, and the assurance that it could not have been better done.

H. R. R.

Atomic Physics. By MAX BORN. Translated from the German Edition by J. DOUGALL. Pp. xii + 352. (London: Blackie and Son.) Price 17s. 6d.

This is a really excellent introduction to practically the whole range of atomic physics, and it deserves the highest praise. The book deals mainly with problems of atomic structure and with recent developments of quantum theory. In addition there is an excellent summary of experimental work in nuclear physics.

The treatment is suited to the needs and capacity of the average honours student. Most of the necessary mathematics is concentrated into a number of appendices which together occupy about one quarter of the whole volume. The main text may therefore be regarded as popular in the best sense of this frequently abused word—that is, it may well appeal to many non-specialist readers who want simple but trustworthy expositions of such topics as quantum statistics and nuclear spin.

As would be expected from an eminent theoretical physicist, Dr Born (to quote from his own preface) has "naturally placed the theoretical interpretation of phenomena well in the foreground". His outlook is however that of a mathematician who has always maintained a close connexion with the laboratory, and his treatment will not be found too austere for the average experimentalist.

The only adverse criticism which can fairly be made is on a matter of detail—the accuracy of the dates which have been inserted "to serve as a historical guide". The intention is excellent; in a book of this size there is obviously no space to spare for historical details, and bare dates can at least serve as reference points for a later survey of the subject. It is however important that the reference points should be correct—more especially just now, when there is in some quarters an evident disposition to rewrite the history of science, and even to re-shape it in terms of ethnographic or political theories. Some of Dr Born's dates are sufficiently inaccurate to mislead quite seriously the young student of the history of physics. For instance (p. 45), in discussing "electromagnetic mass" it is mentioned that

"the effect is the same as if the mass were increased by a part proportional to e^2/a (J. J. Thomson, Heaviside, Searle, about 1900)". In fact, Thomson gave this result (in the *Philosophical Magazine*) as early as 1881, and the period quoted ("about 1900") belongs to a quite different epoch in the history of electrical theory. Again, it would be difficult to justify the attribution (p. 31) of the law of radioactive transformation to von Schweidler in 1905.

We do not wish to stress these points unduly, but the book is of such outstanding excellence that students may well be inclined to regard it as completely authoritative. There is therefore all the more reason for wishing to see it purged of inaccuracies.

Dr Dougall's translation—no doubt aided by a very lucid original text—is very good indeed, and the book is a notable addition to the physics student's select library of essential texts. Modern atomic physics is emphatically not a fit subject for the hack writer, and we are fortunate in getting this text from the pen of a leading original investigator. H. R. R.

Molekülspektren und ihre Anwendung auf Chemische Probleme, II Text, by H. SPONER. Pp. xii + 500. (Berlin: Julius Springer, 1935.) RM. 36, bound RM. 37.80.

The excellence of this volume of Dr Sponer's work comes as no surprise to a reader of the preceding volume (*Tables*), which was reviewed in November 1935 in these *Proceedings*. The completed work is cordially recommended to both spectroscopists and physical chemists. In the first two chapters are brief introductions to (I) the older quantum theory of atomic spectra and (II) the quantum mechanics. The third and longest chapter (205 pages) is devoted to diatomic and polyatomic molecular spectra. However, for reasons which will be evident from the full title of the work, certain aspects of these spectra are either omitted entirely or treated rather briefly. For example, infra-red spectra of diatomic molecules have been adequately covered (apart, of course, from the ever-growing numerical data) by Schaefer and Matossi's book in the same series. Again, the rotational line structure of the various types of electronic bands, the distribution of line-intensities in such bands, and the Zeeman effect have all been treated at some length in several well known books and reviews in recent years, and moreover are of comparatively little significance for the chemical problems to which Dr Sponer gives due prominence in the remaining four chapters (221 pages), namely, the derivation of chemically important quantities from band spectra (chapter IV), chemical binding and valency (chapter V), excitation of molecules by collisions with electrons, atoms, molecules and ions (chapter VI), and other chemical applications of the results of spectroscopic research (chapter VII). There are 87 figures, including a few spectrograms; figures 15–19 and 43 (pp. 51, 54 and 118) would be much improved by the provision of scales of wave-length or wave-number. The usefulness of the tables in vol. I is enhanced by the inclusion in this volume of a 29-page addendum of numerical data and references to papers which appeared up to autumn 1935. Tables and text are thus brought equally up to date.

W. J.

A Class-Book of Magnetism and Electricity. By H. E. HADLEY. Pp. x + 512. (London: Macmillan and Co., Ltd., 1936.) 6s. 6d. net.

This comprehensive text-book is intended mainly to provide a course for School Certificate and Matriculation examinations, but is not confined to their syllabuses. In an introductory chapter on the principal effects of the electric current rather too much is attempted. Most beginners would find difficulty in grasping the analogy between gravitational and electric-current phenomena. The introduction is followed by a full treatment of magnetism, static electricity and current electricity. In the section on magnetism the

fields due to magnets and electric currents are rightly taken consecutively. Then we are given accounts of conduction through gases (including the photo-electric cell and thermionic valve), electric communications, wireless, and television. Practical applications are adequately treated, and the book is up to date. Suggestions for practical work are incorporated with the theory. Many chapters close with interesting historical notes, and there are numerous examination questions and worked examples. The book is well provided with diagrams and is attractively written. It will be welcomed by those who wish for a detailed elementary account of the subject.

A. D. H.

Magnetism. By E. C. STONER. Pp. vi + 136 with 20 diagrams. (Second Edition, Revised 1936. Methuen's Monographs on Physical Subjects.) Price 3s. net.

The appearance of the second edition of this useful little book will be generally welcomed, for it would indeed be difficult to condense more knowledge of the modern aspects of magnetism in a smaller space without serious loss in clarity and important detail. The revision has been carefully done, and on the whole the book reads more easily than the first edition did. It is thoroughly recommended.

L. F. B.

Phenomena in High-Frequency Systems. By A. HUND. (McGraw-Hill Publishing Co., Ltd.) Pp. 642. Price 36s. net.

This book gives a comprehensive account of those portions of physics which have been applied to problems of radio-communication and to a smaller extent of line telephony. One gets the impression that the author has made a thorough search of the literature of the subject, made copious notes, and then arranged them under a dozen or so headings. The result is a book that will probably be consulted occasionally by many workers in search of information on particular points, but few will want to read the whole of it. The scope of the work may be judged by the following typical chapter headings: Space-charge devices, Phase-changers, Frequency-changers, Rectification, Piezo-electricity, The ionized layer, Directive systems, Recurrent networks. The treatment is, generally speaking, encyclopaedic in character, with a huge number of references to original papers. A somewhat jerky style and a singularly uncritical attitude towards the many investigations described make the reading of the book rather heavy work, but the author may fairly claim to have succeeded in his aim "to give a thorough up-to-date discussion of phenomena occurring in high-frequency systems, with many applications to problems arising in communication engineering".

L. H.

The New Acoustics. By N. W. McLACHLAN. Pp. vii + 166. (Humphrey Milford: The Oxford University Press, 1936.) 7s. 6d. net.

The scope of this volume may be gathered from its subtitle, "A Survey of modern developments in acoustical engineering", rather than from its title which might well include the word "applied". The need for some small book to form the counterpart of, say, Foch's more classical *Acoustique* in the Collection Armand Colin has been apparent for some time past to teachers if not to publishers; and it is therefore not surprising that Dr McLachlan, who within the last few months has published two monographs on acoustical topics, should now produce a third dealing with such subjects as anti-submarine devices, microphones, loud-speakers, gramophones, sound films, hearing and deaf aids, and architectural acoustics. As is to be expected the book has a definite engineering bias

and is clearly written and well illustrated, but the reviewer for one would willingly exchange a fifteen-page summary of pre-war acoustics for a few pages additional to, say, the eleven devoted to reverberation and absorption coefficients.

E. J. I.

Das akustische Beugungsgitter und seine Anwendung zur Schallspektroskopie. By ERICH THIENHAUS. Pp. vii + 59 with 21 illustrations. (Leipzig: J. A. Barth.) Price: RM. 2.40.

Prof. Erwin Meyer gave an account of this sound-grating spectrometer in a lecture at Bad Pyrmont two years ago and it has also been described in some detail in the Society's *Progress Reports*, 2, 170 (1936). Suffice it to say here that the grating is made out of a row of equispaced nails round the arc of a circle on the principle of the Rowland grating. The reader who requires details as to its construction will find them given in this brochure together with a complete theory, and typical sound spectra analysed by the apparatus.

E. G. R.

A Fugue in Cycles and Bels. By JOHN MILLS. Pp. 269. (Chapman and Hall.) 13s. 6d.

It is a popular fallacy, fostered by certain universities which provide easy matriculations for would-be graduates in music, that the musician is less endowed with intelligence of worldly matters than the average of his fellow-men. To a certain extent this notion would seem to be fostered by musicians themselves. One suspects that the faint praise with which the fraternity damn Mendelssohn is to a certain extent due to envy for the ease with which this composer mixed dividends and divine inspiration. The author of the book under review tries hard to write down to what he evidently expects to be his readers' low standard of intelligence. "The book is written for those who may wish to know what science is doing to music and what it can do for music", and the author's method of doing this alternates between rather puerile wise-cracking and rather heavy technicalities. He is a telephone engineer and he has some most interesting things to tell us about the development of the telephone and the sense of hearing, but, one feels, less of importance to say about the scientific aspects of music. Thus one would have hoped for a chapter on the acoustics of musical instruments, and the chapter headed "Electrical Music" should have given him the opportunity to describe in detail the various forms of electrical musical instruments now available, a subject which is of great interest to the *modern* musician. As it stands, we rather fear that the book will not reach the public for whom it is meant. Is the author himself a musician? At times he appears to display a facetious contempt for the art. Such a statement as "Music hath power but surprisingly little except when it is played on the big bass drum" is scarcely likely to commend his work to the serious musician.

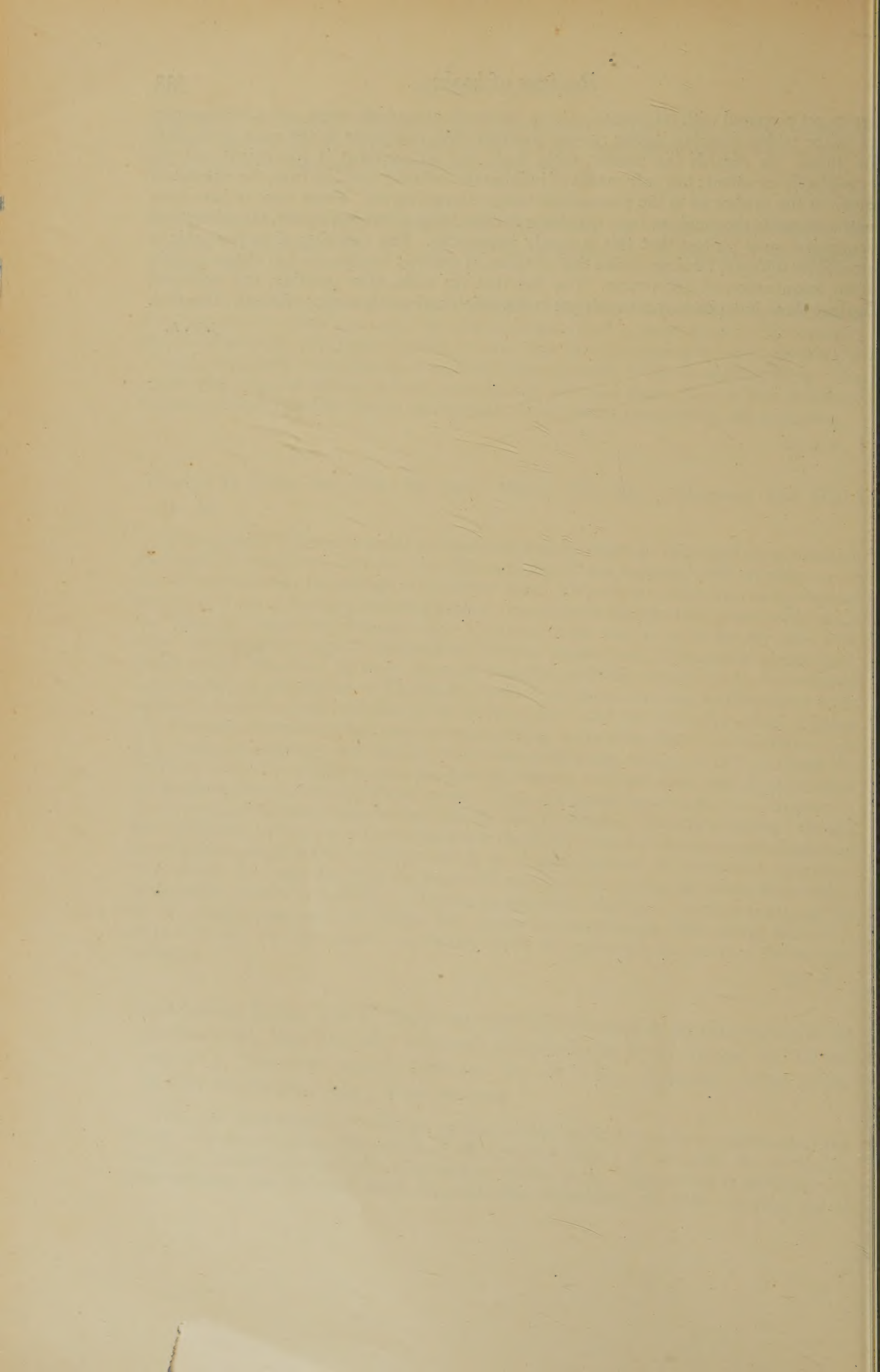
E. G. R.

Mathematical Tables. Vol. 5. Factor table giving the complete decomposition of all numbers less than 100,000. Prepared independently by J. PETERS, A. LODGE and E. J. TERNOUTH and E. GIFFORD. Pp. xv + 291. (London, Office of the British Association, 1935.) Price 20s. net.

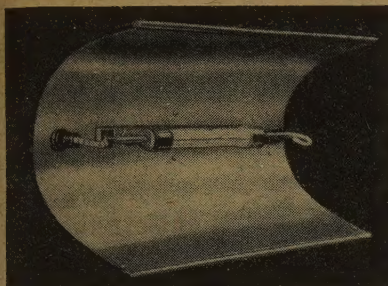
This, the third of the six volumes of *B.A. Tables* to be devoted to a question of the theory of numbers, gives the factors of all numbers from 1 to 100,000. In particular, therefore, it constitutes also a list of primes up to that point. The preface is perhaps even more valuable than the table itself. It gives what is probably the most complete list of

errata yet prepared with reference to earlier tables of comparable scope, and a bibliography of factor tables covering higher ranges, together with references to the main errata lists for them. As regards the present table itself, the arrangement is convenient and the typography excellent; the only means of judging the accuracy must be from the statements given in the preface as to the precautions taken to avoid errors. These seem to have been extraordinarily thorough and one may hope that the table is free from error, though natural scepticism may protest that this is surely impossible. The checking of such a table is peculiarly difficult, because unlike that of tables of analytic functions it can obtain no help from examination of differences. The fact that the table, after printing, was examined against three independent manuscripts is the chief, and surely a very efficient, safeguard.

J. H. A.



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